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A NOTE ON TRAJECTORIES

By

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In §45 et seq. of Murray's Introductory Course in Differential Equations, the discussion on trajectories is somewhat confused. As this otherwise excellent book is deservedly popular with students in this University, it is hoped that the following note will be generally of use. The wording in the book is purposely left unaltered as much as possible.

1. Trajectories, rectangular coordinates. Suppose that

$$f\,(x, y, a)=0. \qquad \ldots \qquad \ldots \qquad (1)$$

is the equation of the given system of curves, a being the arbitrary parameter; and that α is the angle at which the trajectories are to cut the given curves. The elimination of a from (1) gives an equation of the form

$$\phi\left(x, y, \frac{dy}{dx}\right)=0. \qquad \ldots\ldots \qquad \ldots \qquad (2)$$

the differential equation of the family of curves.

Now through any point (x, y) there pass (i) a curve of the given system and (ii) one of the trajectories, cutting each other at an angle α. If m is the slope of the tangent to the trajectory at this point, then

$$m=\frac{\frac{dy}{dx}-\tan\alpha}{1+\frac{dy}{dx}\tan\alpha} \qquad \ldots \qquad \ldots \qquad (3)$$

$$\therefore\ \frac{dy}{dx}=\frac{m+\tan\alpha}{1-m\tan\alpha} \qquad \ldots \qquad \ldots \qquad (4)$$

$$\therefore\ \phi\left(x, y, \frac{m+\tan\alpha}{1-m\tan\alpha}\right)=0 \qquad \ldots \qquad (5)$$

is the equation satisfied by m. But by definition m is $\frac{dy}{dx}$ for the trajectory; hence the differential equation of the system of trajectories is obtained by substituting $\frac{dy}{dx}$ for m in it; (x and y

being common to the original curve and the trajectory). This gives

$$\phi\left(x,\ y,\ \frac{\dfrac{dy}{dx}+\tan\alpha}{1-\dfrac{dy}{dx}\tan\alpha}\right)=0 \qquad \dots \qquad (6)$$

for the differential equation of the system of trajectories.

2. In the book, the differential equation is obtained by substituting the value of m given by (3) for $\frac{dy}{dx}$ in (2); the reason for this substitution is not clear and one would expect the method to give a wrong equation. But the equation coincides with (6) if $-\alpha$ is written for α. This shows that it is the equation of the other set of trajectories cutting the given curves at angle α *on the other side.* But it is not the equation of the trajectories which the book sets out to find.

3. The complete equation of both sets of trajectories is therefore

$$\phi\left(x,\ y,\ \frac{\dfrac{dy}{dx}\pm\tan\alpha}{1\mp\dfrac{dy}{dx}\tan\alpha}\right)=0. \qquad \dots \qquad (7)$$

It may be noted that the author uses the correct equation (6) given above in solving Ex. 1 on page 57 and not the result given by him, He however fails to notice the other solution viz. $x^2+y^2=2c(my-nx)$, corresponding to the other set.

4. **Orthogonal trajectories.** When α is a right angle both sets of trajectories coincide and the result given in the book is correct, but the argument is defective and should be replaced by the following:

If α is a right angle, $m=-\frac{dx}{dy}$, i. e. $\frac{dy}{dx}=-\frac{1}{m}$; and hence the equation satisfied by m is

$$\phi(x,\ y,-1/m)=0. \qquad \dots \qquad \dots \qquad (8)$$

∴ The differential equation of the orthogonal trajectories, obtained by writing dy/dx for m in (8), is

$$\phi(x,\ y,-1/(dy/dx))=0,$$

or more simply $\phi(x,\ y,-dx/dy)=0. \qquad \dots \qquad \dots \qquad (9)$

5. **In polar coordinates,** (§46), if the differential equation of the given curves is

$$\phi(r.\ \theta,\ dr/d\theta)=0. \quad \dots \quad \dots \quad (10)$$

and m is the tangent of the angle between the radius vector and the tangent to the trajectory at the point of intersection, $m=\tan\ (\phi\pm\alpha)$, where ϕ is the angle between the radius vector and the tangent to the given curve, i. e. $\phi=\tan^{-1}\ (rd\theta/dr)$

$$\therefore \quad \frac{rd\theta}{dr}=\frac{m\mp\tan\alpha}{1\pm m\tan\alpha}, \text{ or } \frac{dr}{d\theta}=\frac{r\,(1\pm m\tan\alpha)}{m\mp\tan\alpha}$$

The equation satisfied by m is accordingly

$$\phi\left(r,\ \theta,\frac{r(1\pm m\tan\alpha)}{m\mp\tan\alpha}\right)=0. \quad \dots \quad (11)$$

Hence the required differential equation is obtained by substituting $rd\theta/dr$ for m in (11), and is thus

$$\phi\left(r,\ \theta,\ \frac{r\left(1\pm\dfrac{rd\theta}{dr}\tan\alpha\right)}{r\dfrac{d\theta}{dr}\mp\tan\alpha}\right)=0. \quad \dots \quad (12)$$

6. The equation of the orthogonal trajectories is similarly seen to be

$$\phi\left(r,\ \theta,-r^2\frac{d\theta}{dr}\right)=0, \quad \dots \quad \dots \quad (13)$$

obtained by writing $r\ d\theta/dr$ for m in $\phi\ (r,\ \theta,-rm)=0$, which is the equation satisfied by m when α is a right angle.

Equations (9) and (13) may be obtained as the limiting forms of (7) and (12) as $\alpha\to\pi/2$.

[*Received: 15th August 1938*]

DESCARTE'S RULE OF SIGNS

By

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It is difficult to find, in the whole range of Higher Mathematics, a theorem whose proof excels that of Descarte's Rule of Signs in sheer subtlety of argument. It is no wonder that many authors including Burnside and Panton, the joint authors of the classical work on the theory of equations have failed to present the argument in a convincing manner. Mr. Rama Sastry has published a proof in a recent issue of "*The Mathematics Students*" where he rightly complains that many of the existing proofs are mere verifications of the theorem in particular cases. The following proof strengthens and clarifies his argument at many stages and reaches a more precise statement of the theorem. It is a modified form of the one given in my book, 'Higher Algebra and Trigonometry'. I am now seeking the courtesy of the Journal in order to rescue it from the obscurity of the book in which it lies buried.

Lemma: The number of changes of sign in the distributed product $(x-a)\,P(x)\ (a>o)$ exceeds the number of changes of sign in the polynomial $P(x)$ by an odd number.

Let us suppose that the sequence of signs in $P(x)$ is

$$+ \quad + \quad + \quad - \quad + \quad + \quad - \quad - \quad + \quad + \cdot$$

Now noting only the signs that occur in the process of multiplication, we have

$$\begin{array}{ll} xP(x) & \equiv + \; + \; + \; - \; + \; + \; - \; - \; + \; + \; 0 \quad \text{1st row} \\ -aP(x) & \equiv 0 \;\cdots\;\cdots\;\cdots\;\cdots\;\cdots\;\cdots\;\cdots\;\cdots\;\cdots\; - \quad \text{2nd row} \\ (x-a)P(x) & \equiv + \;\cdots\;\cdots\; - \; + \;\cdots\; - \;\cdots\; + \;\cdots\; - \quad \text{3rd row} \end{array}$$

Now the first row of signs is completely known. Although signs in $-aP(x)$ are also known, since P (x) may be incomplete, we can not arrange the second row so as to write the signs of like powers in the first two rows, in the same vertical column. The last sign in the second row, however, is opposite to the last sign in the first row, hence in our case, it must be negative. Again only some signs in the third row are determinate. The first sign in the third row is clearly positive, since the degree of $xP(x)$ is higher by one than the degree of $-aP(x)$. Now either there is no term which can be written under the second term or there is a negative term. Hence the corresponding sign in the third row is indeterminate. Such a situation arises whenever a sequence of two like signs occurs in the first row. In this case the sign in the third row corresponding to the second of the two like signs is indeterminate. We indicate an indeterminate sign by dots.

Now let us consider the fourth sign in the first row. Either there is no term in $-aP(x)$ which can be written under it or there is a negative term which arises by the multiplication of $-a$ and the preceeding positive term. In either case the corresponding sign in the third row is negative. Similarly whenever we have a sequence of two unlike signs in the first row, the second of the two unlike signs persists in the third row.

As a result of these remarks we conclude that whenever a set of positive signs is followed by a negative sign, in the first row, the corresponding set in the third row begins with a positive sign and ends with a negative sign, the intervening signs being indeterminate. A similar result follows when a set of negative signs is followed by a positive sign in the first row.

We now observe that in any sequence of signs in which the extreme signs are opposite the number of changes of sign must be odd. It is thus seen that for every change of sign in the first row there is a set of odd number of changes of sign in the last row. Further, the last sign in the third row must be opposite to the last sign in the first row ; hence in our case it must be negative. This sign introduces an *additional* odd number of changes of sign.

We finally conclude that the number of changes of sign in the last row must exceed the number of changes of sign in the first row by an odd number. Hence the lemma.

Now suppose $P(x)$ is the product of the factors corresponding to negative and pairs of conjugate complex roots. Then every time we multiply $P(x)$ by a factor of the form $x-a$ which corresponds to a positive root we introduce an odd number of sign. Hence we deduce the Rule : There can not be more positive roots than there are changes of sign in an equation.

A more precise statement of the theorem may be reached thus : A factor corresponding to a negative root is of the form $(lx+m)$ where l and m are of the same sign and a factor corresponding to a pair of conjugate complex roots is of the form $(x-p)^2+q^2$. Hence P (x) must be of the form.

$$\Pi\ (lx+m)\ \Pi\ [(x-p)^2+q^2]$$

This shows that the extreme signs in the sequence of signs in P (x) are alike. Now it is easily seen that in such a sequence the number of changes of sign must be even. Hence the above rule may be stated more precisely thus :

The number of changes of sign in $f(x)$ either equals or exceeds by an *even* number the number of positive roots of the equation $f(x)=0$, $f(x)$ being a polynomial.

[*Received 1st June 1938.*]

DEMLO NUMBERS

By

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Khare's Wada, Camp Deolali.

(Communicated by Prof. M. L. Chandratreya)

[Mr. D. R. Kaprekar is a B.Sc. of the Bombay University. While very young he was attracted by the properties of numbers and worked at them whenever he could find time. He has a knack of discovery in spite of his not being acquainted with the general development of the theory of numbers. His discoveries within the last 15 years though 'too elementary' deserve attention. Among many other wonderful properties of numbers, he has developed systematically Demlo numbers as he calls them and his later researches are very noteworthy. He is busy at present in the theoretical expression of his work. A short summary only of a part of his work is given here.]

Definition:—A Demlo number consists of three parts when the digits are taken in order from left to right. First part called M and last part called P such that M+P= one and the same digit repeated some number of times. The middle part is formed of the repeated digit taken any number of times. e.g.

23777754 has M=23, P=54, M+P=77. Here 7 is repeated twice. The middle part is 7 repeated four times. This number will be denoted as

$$\left(\begin{array}{c} M \\ r|n \\ P \end{array}\right) \quad \text{e.g. the number above would be} \quad \left(\begin{array}{c} 23 \\ 7|4 \\ 54 \end{array}\right)$$

Sometimes the two parts M and P are absent in such a number and then it can be represented by $(r]n)$. It is obvious that M and P must have usually the same number of digits but sometimes M may have one digit less in which case it is properly written by introducing a zero when necessary. Thus 87666579 has M=87, P=579, M+P=666 and the number is written as $\begin{array}{c} 087 \\ 6|3. \\ 579 \end{array}$

Classification:—Demlo numbers may be classified according to the different properties they possess.

(1) Linear Demlo Numbers of the type $(r]n)$

(2) Binary Demlo Numbers of the type

$$\begin{array}{c} M \\ \overline{\underline{r}}\rvert\, n \\ P \end{array}$$

(3) Male Demlo Numbers of the type

$$\begin{array}{c} M \\ \overline{\underline{9}}\rvert\, n \\ P \end{array}$$

(4) Female Demlo Numbers contain 3 or 6 as the repeated digit.

(5) Neutral Demlo Numbers in which one digit is repeated, (other than 9, 3 and 6)

(6) Just saturated Demlo Numbers in which one digit only occurs in the repeated part

(7) Oversaturated Demlo Numbers in which more than one digit occurs in the repeated part.

(8) Complementary Demlo Numbers in which the repeated parts are absent.

(9) Unsaturated Demlo Numbers in which the repeated part is not only absent but is present in a negative way.

(10) Wonder Demlo Numbers in which M and P contain some of the digits 1, 2, 3......9 beginning from 1 in order and the same in the reverse order; thus M = 1234, P = 4321 and will be

$$\begin{array}{c} 1234 \\ \overline{\underline{5}}\rvert\, n \\ 4321 \end{array}$$

(11) Consecutive Demlo Numbers such as

$$\begin{array}{c} M \\ n \\ P \end{array} \quad \text{and} \quad \begin{array}{c} M-1 \\ n \\ P+1 \end{array}$$

(12) Exchanged Demlo Numbers such as

$$\begin{array}{c} M \\ \overline{\underline{r}}\rvert\, n \\ P \end{array} \quad \text{and} \quad \begin{array}{c} P \\ \overline{\underline{r}}\rvert\, n \\ M \end{array}$$

WAYS OF OBTAINING DEMLO NUMBERS

The Demlo Numbers are found to occur in some of the following peculiar processes.

(1) Any number mulitiplied by $(10^\circ+10^1+10^2+....10^n)$ gives a Demlo Number. The equivalent process is to multiply

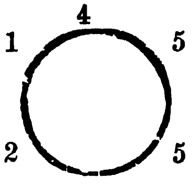
any number by $(\underline{\overline{1}}|n)$ i.e. a number formed of digit 1 repeated any number of lines. An interesting way of getting the result is to write down the number diagonally as in the process of multiplication called the diagonal process hereafter.

e.g. $365(10^0+10^1+10^2+10^3)=365\times1111$

$$= \begin{array}{r} 365 \\ 365 \\ 365 \\ 365 \\ \hline 405515 \end{array} \qquad = \left(\begin{array}{c} 40 \\ \overline{5}\,\rvert\,2 \\ \overline{15} \end{array}\right).$$

(2) Exchange some equal digits from the two ends of any given number and subtract the smaller from the greater. *e.g.* 53824612 gives when 53 and 12 are exchanged 12824653. Their difference is 40999959 $= \left(\begin{array}{c} 40 \\ \overline{9}\,\rvert\,4 \\ \overline{59} \end{array}\right)$ = a Demlo Number.

(3) Cyclic Process consists in writing down any number along the circumference of a circle and the numbers formed by taking every digit as the first and the other digits in order and, then summing them all. e.g. 45321.



$$\text{Here}\quad \begin{array}{c} 4\,5\,3\,2\,1 \\ 5\,3\,2\,1\,4 \\ 3\,2\,1\,4\,5 \\ 2\,1\,4\,5\,3 \\ 1\,4\,5\,3\,2 \end{array} \quad \text{Sum} = 1\,6\,6\,6\,6\,5$$

a Demlo Number.

(4) H—Theorem:—The Theorem states that if N is any number $N+(N-1)+8N+10C=(\underline{\overline{9}}|n)$ where C is what is called the complementary number of $(N-1)$ with respect to the digit 9 and n is the number of digits in 8N; (the complementary number of any given number with respect to a digit r is the number obtained by subtracting the number from a number $\underline{\overline{r}}|\,n$ containing as many digits as the given number. Thus complementary of 3621 with respect to seven is $7777-3621=4156$. The value of r is not necessarily restricted to the digits from 1 to 9.)

e.g., $N=7425$, $N-1=7424$ $8N=59400$
$10C=25750$ Sum $=99999$ $=(\underline{\overline{9}}|5)$.

The theorem has been generalished thus:—$N+(N+H-10)+8N+10C+10(H-10+1)=\underline{\overline{H}}|n$ where H is any number and C is the complementary of $N+H-10$ with respect to H. Here also n is the number of digits in 8N.

(5) Processes of conical tables

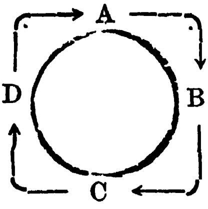
Table No. 1	Table No. 2
$1 \times 9 + 2 = 11$	$0 \times 9 + 8 = 8$
$12 \times 9 + 3 = 111$	$9 \times 9 + 7 = 88$
$123 \times 9 + 4 = 1111$	$98 \times 9 + 6 = 888$
$1234 \ldots \times 9 + \therefore = 111 \ldots$	$987 \times 9 + 5 = 8888$
etc.	*etc.*

A number of tables having such peculiar propecties can be constructed.

(6) D—Theoem :—The theorem states that if A and B are two numbers of the same number of digits and C and D are their complements respectively with respect to 9, then.

$A \times B + B \times C + C \times D + D \times A + A + B + C + D = (\overline{9}|2k)$ where k is the number of digits in A or B.

The rule may be expressed by



$$+ \ A+B+C+D \ = (\overline{9}|2k)$$

the double products being taken in order beginning with any number.

The theorem has been generalised. If A and B are two numbers of the same number k of digits and C and D are their conplements respectively with respect to a number m, then

$$A \times B + B \times C + C \times D + D \times A + A + B + C + D +$$
$$\left(\overline{m}\,\middle|\,k\right) + \left(\overline{\overline{9-m}}\,\middle|\,k\right) = \left(\overline{m}\,\middle|\,2k\right).$$

A still more generalised form has also been established.

(7) If any series of increasing numbers are taken such as a, b, c, d, e say where $a<b<c<d<e$ and if the differences from e of all others are taken in order from a, b, c, d and all these numbers a, b, c, d, e, $e-a$, $e-b$, $e-c$, $e-d$ are written in diagonal order then the resulting sum is a Demlo Number *e.g.*

271, 324. 465, 612 are increasing numbers. The differences from the last are 341, 288, 147.

Writing diagonally

$$\begin{array}{r} 271 \\ 324 \\ 465 \\ 612 \\ 612 \\ 612 \\ 341 \\ 288 \\ 147 \\ \hline \underline{17988}\ 9\ \underline{82011} \end{array} = \left(\begin{array}{c} 17988 \\ \underline{\overline{9}}\,|\,1 \\ 82011 \end{array}\right)$$

Here it can be seen that 612 the greatest number is repeated in the process thrice. It can be repeated any number of times. The process will be referred to as the Haphazarded Process.

(8) If the recurring decimal fraction part of $\frac{1}{N}$ where N is prime or product of two or more primes is multiplied by N, then we get a Demlo Number

Thus $\frac{1}{7} = \cdot 142857 \cdot$ Here $142857 \times 7 = 999999$

or $\frac{1}{657} = \cdot 00152207 \cdot$ Here $152207 \times 657 = 99999999$

Not only this but every recurring decimal portion is itself a Demlo number. Thus in the above

$$142857 = \left(\begin{array}{c} 142 \\ \underline{\overline{9}}\,|\,0 \\ 857 \end{array}\right), \qquad 152207 = \left(\begin{array}{c} 15 \\ \underline{\overline{2}}\,|\,2 \\ 07 \end{array}\right),$$

$\frac{1}{17} = \cdot 05882352 \quad 9411647 = \left(\begin{array}{c} 05882352 \\ \underline{\overline{9}}\,|\,0 \\ 94117647 \end{array}\right)$, a complementary Demlo Number.

Take $\frac{1}{31} = \cdot 032258064516129$. This gives an unsaturated Demlo Number. The test for such a number is to divide the number in three parts and if we add together thus

$$\begin{array}{r} 03225 \\ 80645 \\ 16129 \\ \hline 99999 \end{array} = \left(\underline{\overline{9}}\,|\,5\right),$$

We get a linear demlo number.

Properties of Demlo Numbers

The general theory of these Demlo Numbers has been developed, showing how different arithmetical processes are applied and how the resulting values can be easily put down. Only a few peculiarities of these numbers are given below. The full exposition with the theoretical explanation has been done and need not be given here at present.

(1) Peculiar property of Wonder Demlo Numbers. Take such number say

$$\begin{array}{c} 12345 \\ \underline{\overline{6}}\,|\,1 \\ 54321 \end{array}$$

and let us multiply it by 162. Then the product is

$$1\ \boxed{99999}\ 6\ \boxed{00000}\ 2.$$

It means ; write 1, 6, 2 separated and write 5 nines and 5 zeros between and we have the product. This process of writing down the product is called the Partition and Insertion Process. Take another example. 1234567654321 is a wonder number. To multiply it by 207, we just write 2, 0, 7 in order and insert 6 fives and 6 fours between thus

$$2\ \boxed{555555}\ 0\ \boxed{444444}\ 7.$$

and 2 555555 0 444444 7 is the product. It can be shown that there are only twenty five of such numbers and they are 108, 117, 126, 135, 144, 153, 162, 207, 216, 225, 234, 243, 009, 018, 027, 036, 045, 054, 063, 072 and 081. There are very simple rules to find out the repeated digits to be inserted.

(2) A few numbers when they are multiplied by 1, 2, 3, 4... in order and the resulting numbers are added diagonally, show some special properties. Thus 657 and 324 give.

$$\begin{array}{r} 657 \\ 1314 \\ 1971 \\ 2628 \\ 3285 \\ 3942 \\ \cdots\cdots \\ \hline \cdots\cdots 88888897 \end{array} \qquad\qquad \begin{array}{r} 324 \\ 648 \\ 972 \\ 1296 \\ 1620 \\ 1944 \\ \cdots\cdots \\ \hline \cdots\cdots 0000004 \end{array}$$

This repetition and the reasons for it can be explained by the general Theory of Demlo number.

(3) Recurring part obtained by dividing unity by some *Demlo Numbers show another peculiarity. Thus 891 is a Demlo*

Number

$\frac{1}{891} = \cdot 0011223344556677 89$

$\frac{1}{8991} = \cdot 000111222333444555666777889$

$\frac{1}{89991} = \cdot 000011112222 \ldots\ldots\ldots\ldots\ldots 8889$

The result may be written generally as

$$\frac{1}{\left(8\;\overline{9}\rfloor n\;1\right)} = \cdot\left(\overline{0}\,\middle|\,n+1\right)\left(\underline{1}\,\middle|\,n+1\right)\left(\overline{2}\,\middle|\,n+1\right)\left(3\,\middle|\,n+1\right)\ldots\left(8\,\middle|\,n\right)9$$

$$= \cdot\left(\boxed{0, 1, 2, 3, 4, 5, 6, 7}\;n+1\right)\left(\underline{8}\,\middle|\,n\right)$$

(4) Given any fraction the recurring part of the fraction can be calculated without going through the process of division. It gives thus a simpler process for transforming any fraction into a recurring decimal. Take $\frac{1}{7}$. In order to transform it multiply 7 successively by 5, 5 × 5, 5 × 5 × 5 and apply the diagonal process. Thus

```
                   07
                  35
                175
               875
             4375
           21875
         109375
        546875
      2734375
    -------------------
.........2857 | 142857
```

Here it will be seen that 142857 will be repeated in the process.

Take $\frac{1}{19}$. Here the number 1 will be successively multiplied by 2 and the diagonal process is used and we get

............421052631578947368421

where the underlined quantity is the recurring part of $\frac{1}{19}$. The theory and mathematics of Demlo Numbers enables us to construct these recurring parts orally, by choosing a proper number and a proper multiplyer for any given fraction.

(5) Squares and cubes of Demlo Numbers have also very interesting features. Thus

$$\begin{array}{rrrrr}
(1833315)^2 = 336 & 1 & 0438 & 8 & 9225 \\
(18333315)^2 = 336 & 11 & 0438 & 88 & 9225 \\
(183333315)^2 = 336 & 111 & 0438 & 888 & 9225
\end{array}$$

Thus generally

$$\left(\begin{array}{l}18\\ \overline{3}\big|n\\ 15\end{array}\right)^2 = 336\left(\underline{\overline{1}}\big|n-2\right)0438\left(\underline{\overline{8}}\big|n-2\right)9225$$

Here 336, 0438, 9225 are called constants of the quantity and 1 and 8 are the repeaters. A number of equations have been prepared and definite rules are laid down which enable us to find these constants and these repeaters for the square of any given Demlo number.

The square and product of any linear Demlo Number can be set down by only a table of 23 constants. The same table also enables us to write down at once the product of two Demlo Numbers of the same length.

Let us take the example of the cube of a Demlo Number.

$$\left(\begin{array}{l}17\\ \overline{9}\big|n\\ 82\end{array}\right)^3 = 5831\left(\underline{\overline{9}}\big|n-3\right)82504\left(\underline{\overline{0}}\big|n-3\right)17495\left(\underline{\overline{9}}\big|n-3\right)$$
$$-94168$$

Here there are four constants and three repeaters. These constants and their properties and determination also find a place in the discussion of the general theory. It is interesting to see that the sum of the constant parts in the squares and cubes display special features. In the two examples given above

$$\begin{array}{r}336\\0438\\\underline{9225}\\9999\end{array}\qquad\qquad\begin{array}{r}5831\\82504\\17495\\\underline{94168}\\199998\end{array}$$

the sums are Demlo Numbers.

[Even on the surface these properties appear to be very interesting and Mr. Kaprekar deserves credit for the work that he is doing and has already done. Because of these properties he has been able to do a number of feats in calculation which appear to be very simple when the Demlo Numbers are taken into consideration. We hope that Mr. Kaprekar publishes his work early in this connection. M. L. C.]

SUSCEPTIBILITY CONSTANTS OF THALLIUM IN DIFFERENT STATES

By

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The ferromagnetic elements, the inert gases and some of the elements which exist at room temperature as gases have been critically and extensively examined by various authors. Honda and Owen[1], in a series of investigations have studied the magnetic properties of about sixty elements at various temperatures. Their results combined with those of later workers enable us to survey the magnetic behaviour of many elements. Contrary to the general behaviour, the susceptibility of many paramagnetics either increases with temperature or is constant while that of many diamagnetics varies with temperature considerably.

In metals the free or loosely bound electrons play an important part in super-imposing a paramagnetic effect on the diamagnetism, while in non-metals the phenomenon of this nature could not be generally traced. Further, it is unsafe to suppose that a metal regarded as an aggregate of atoms should possess characteristics indicated by those of the constituents as there are free electrons between component atoms. Paramagnetic atoms, such as thallium, copper and silver, are found to be diamagnetic in the metallic state.

The existence of elements in various states, such as solid, liquid and vapour, is open to fresh orientation in their magnetic properties. Although the polyatomic molecules of sulphur and selenium in the liquid and solid states are diamagnetic, their diatomic molecules in the vapour state have been found by Neel[2], Bhatnagar[3] and others to be paramagnetic. It appears, therefore, probable that a thermomagnetic investigation of thallium may throw some light on this unique phenomenon.

The susceptibility constants for thallous thallium obtained by Kido[4] and Trew[5] are not in agreement with the theoretical ones. The experimental values are considerably lower than the theoretical ones, indicating a discrepancy between theory and experiment. A comparative study of the whole subject has been undertaken in this investigation.

EXPERIMENTAL

The specific susceptibility of the salts has been determined by a suitably modified form of Gouy's balance[6]. The calculations were made according to the equation :

$$xd_2 = \frac{1}{md_2}\left[(xd_1\ md_1 - x_a m_a d_1)\frac{wd_2}{wd_1} + x_a m_a d_2\right]$$

where the letters have the usual significance.

For higher temperature-measurements of thallium, an electric furnace made of a double filament of coiled nichrome wire was used. The temperatures were measured with the help of a pyrometer.

Preparation of pure Thallium:—

The metal was dissolved in dilute sulphuric acid, the solution filtered and allowed to crystallise. Thallium sulphate thus formed was twice recrystallised from water. 5% solution of this substance was made slightly acidic with sulphuric acid and treated with hydrogen sulphide to remove traces of mercury, silver, arsenic, antimony and bismuth. The solution was filtered and treated with aq. ammonia to remove traces of iron and aluminium. The filtrate thus obtained was evaporated until crystals of thallous sulphate were separated. Thallium was prepared by the electrolysis of the saturated solution of the above described sulphate, using platinum electrodes. The anode was placed near the bottom of the beaker while the cathode merely dipped beneath the surface. The red deposit of peroxide at the anode remained at the bottom and therefore did not contaminate the spongy mass of thallium deposited above on the cathode. A current of about 0·5 amp. was used. Thallium was removed at frequent intervals and rinsed thoroughly with pure and air-free water. It was then kept under vacuum, the evacuation being driven to a point when the cathode ray discharge practically ceased. The same process with the necessary precautions was repeated while sealing it in a silica tube. Care was also taken to remove any air adsorbed on the walls of the tube before the sample was introduced. Similarly most of the thallium salts were prepared and purified in the laboratory. In every case, the physical properties were determined and compared with those given in standard tables. Only those substances which proved to be quite pure, after going through the exhaustive process of analysis, were employed for the magnetic measurements.

EXPERIMENTAL RESULTS

Specific Susceptibility of Thallium Metal

TABLE I.

Authors	Specific Susceptibility $-x. 10^6$
Honda[7]	0.25
Owen[8]	0.23
W. de Haas & P. M. Van Alphen[9]	0.215
S. R. Rao & Subramaniam[10]	0.244
A. W. David & J. F. Spencer[11]	0.223
Observed	0.228

TABLE II

Thermomagnetic Readings of Thallium Metal

(Transforms itself into vapours at higher temperatures in vacuum)

Tube A. Weight-empty tube = 2.1235 gms.

Wt. of Thallium contained in it. = 0.0182 g.m.

Temperature°C.	Combined magnetic pull in Grams (Pull of Silica tube plus Pull due to Thallium metal)	
22	0.0023.	solid
590	0.0012.	vapour
692	0.0013.	„
800	0.0016.	„
1020	0.0023.	„

Tube B. Wt. of empty tube = 1.5215 gms.

Wt. of thallium contained in it = 0.0178 gms.

22	0.0011	solid
590	0.0000	vapour
692	0.0002	„
800	0.0007	„
1020	0.0010	„

Tube C. Wt. of empty tube = 1.8925 gms.

Wt. of thallium contained in it = 0.0168 gms.

22	0.0015	solid
590	0.0005	vopour
692	0.0007	„
800	0.0011	„
1020	0.0015	„

(It has been shown by Bhatnagar, H. Lessheim & M. L. Khanna (Proc. Ind. Acd. Sci. Sept. 155, 156 pp., 1937) that the measurements on the empty and evacuated tubes showed not the slightest change in the forces exerted by the magnet between room temperature and 1100° C; the changes in the fields, which were due to a slight warming of the pole pieces and due to heating air between them were apparently very minute and below the sensitivity of the balance compared with the considerable changes in the forces when the tubes were full of thallium vapours at higher temperatures. It is evident from this that the changes in the magnetic pulls that were taking place, were due to those of thallium vapours only. Due care was taken to evacuate the silica tubes completely as slightest presence of oxygen would have vitiated the results)

TABLE III

Specific Susceptibilities of Thallium salts.

Substance.	Specific Susceptibility. $-x \cdot 10^6$	Specific Susceptibility from other sources $-x \cdot 10^6$
TlCl	0.241	0.242 Kido[12]
		0.230 Klemm & Tilk[13]
		0.241 Trew[14]
		0.190 Tables
TlBr	0.246	0.225 Trew
TlI	0.264	0.248 „
$TlNO_3$	0.2136	0.212 „
		0.200 Tables
Tl_2O	0.1927	
Tl_2SO_4	0.225	0.223 Trew
		0.250 Tables
Tl_2CO_3	0.216	0.217 Trew
Tl_2S	0.228	0.202 „
TlCNO	0.2158	0.225 „
TlCNS	0.2654	0.254 „
$TlOOC.\ CH_3$	0.2555	0.262 „
$TlOOC.\ C_5 H_6$	0.3255	0.344 „

TABLE IV

Susceptibility Constants of Thallium Ion

Substance	Susceptibility Constants		
	Molecular susceptibility observed $-XM. 10^6$	Values for − ve radicals and their sources $-X. 10^6$	Susceptibility constants $-X. 10^6$
TlCl	57·8	23·1 (Hoccart)	34·7
	57·8	22·1 (Kido)	35·7
	57·8	20·4 (Ikenmeyer)	37·4
	57·8	20·1 (Pascal)	37·7
	57·8	19·85 (Bhatnagar)	37·95
			Mean 36·69
TlBr	69·83	33·9 (Hoccart)	35·93
	69·83	34·7 (Kido)	35·13
	69·83	34·8 (Ikenmeyer)	35·03
	69·83	30·5 (Pascal)	39·33
	69·83	32·5 (Reichender)	37·33
	69·83	31·4 (Farquharson)	38·93
			Mean 36·94
$TlNo_3$	56·92	14·2 (Pascal)	42·72
	56·92	20·1 (Kido)	36·82
			Mean 39·77
TlI	87·46	49·5 (Hoccart)	37·96
	87·46	53·2 (Kido)	34·26
	87·46	44·6 (Pascal)	42·86
	87·46	49·25 (Ikenmeyer)	31·21
			Mean 38·32
Tl_2O	81·83	4·6 (Pascal)	38·61
	81·83	13·7 (Kido)	34·06
			Mean 36·33
Tl_2SO_4	113·6	33·6 (Pascal)	40·00
	113·6	39·0 (Kido)	37·3
			Mean 38·65

TABLE IV *(continued)*

Susceptibility Constants of Thallium Ion

Substance	Susceptibility Constants		
	Molecular susceptibility observed $-XM. 10^6$	Values for $-$ ve radicals and their sources $-X. 10^6$	Susceptibility constants $-X. 10^6$
Tl_2CO_3	101·25	22·2 (Pascal)	39·52
	101·25	28·1 (Kido)	36·57
			Mean 38·04
Tl_2S	99·54	15·0 (Pascal)	42·27
	99·54	27·4 (Kido)	36·07
			Mean 39·13
TlCNO	53·16	25·21 (Kido)	27·95
	53·16	16·2 (Trew)	36·96
TlCNS	69·61	30·0 (Trew)	39·61
	69·61	38·0 (Kido)	31·61
$TlOO\ CH_3$	67·32	28·9 (Pascal)	38·42
	67·32	32·0 (Kido)	35·32
			Mean 36·87
$Tl.O.O.C._6H_5$	105·6	69·2 (Pascal)	36·4

DISCUSSION OF RESULTS

The specific susceptibility $-0{\cdot}228{\cdot}10^{-6}$ of thallium metal closely corresponds to those of Owen and David and Spencer, while it differs slightly from those of other investigators such as Honda, S. R. Rao and de Haas (see Table I). From the thermomagnetic measurements (Table II) it is evident that thallium becomes paramagnetic in the vapour state. However, the thallium vapours begin to attack glass with the rise of temperature, *i.e.* at about 1020°C. with the result that it regains its former diamagneti No quantitative results could therefore be obtained. The trend o readings, however, shows the existence of paramagnetism of thallium in the vapour state. It has been deduced from an examination of the various physical properties that thallium is polyatomic in the solid state and monoatomic in the vapour state. The fact that thallium becomes paramagnetic in the vapour state clearly establishes the above statement from the magnetic point of view. The diamagnetism of thallium in the solid state indicates that the free electrons in the outer orbit are combined in such a way that the electron spins compensate each other with the formation of polyatomic thallium molecule.

Thallium Salts:—

From the survey of the physical properties such as degree of dissociation and electrical conductivity of the thallium salts, it is seen that they are strong electrolytes. In the determination of the susceptibility constants of thallous thallium, Pascal's atomic values given in the tables cannot be used as stated by Trew. The atomic susceptibility values due to Pascal are primarily used on measurements of homopolar compounds. They are appropriate for atoms in combination, but the values assigned differ widely from those for free atoms or quasi-independent ions. It has, therefore, been found desirable to calculate the susceptibility constants of thallous thallium by subtracting the different values of the anions from their molecular susceptibilities. The method adopted by Trew cannot be considered to be valid in strongly electrovalent salts of thallous thallium in finding the ionic constants. The observed mean susceptibility constants are not altogether different from those that are obtained by Trew. The constants determined by Kido are slightly higher. However, the experimental values are considerably lower than the theoretical one $(-63 \cdot 19 \times 10^{-6})$ obtained by Trew following Slater's method. Susceptibility of a heteropolar salt, both as a solid and in solution is considered to be the sum of the susceptibilities of positive and negative ions:

$$X_m = X_{ion}{}^{+} + X_{ion}{}^{-}$$

Many a time, the states of ions are different under different conditions. The ionic values in the solid and dissolved states would be less than those in the free state as the effective spread of the electric density distribution is very much limited with the result that the radii of the ions on which diamagnetism depends are deformed. Similar explanations have been put forth by Hocart[15], Brindley[16], Goldschmidt[17], and Trew[18]. Trew has made definite distinctions in the ionic values obtained by subtracting the ionic values of monovalent, divalent and organic anions from their molecular susceptibilities. However, he is not justified in drawing these conclusions as the method adopted by him in obtaining the ionic values is not completely accurate.

The writer sincerely thanks Professor S. S. Bhatnagar for his great interest as well as his kind advice in the course of the present investigation.

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COEFFICIENTS OF VISCOSITY OF GASES

By

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In 1923, Wagstaff[1] suggested a method for measuring the coefficient of viscosity of air and in these investigations his apparatus has been improved and applied to the measurements of viscosity coefficients of air and of carbon di-oxide, nitrogen and oxygen. At first experiments were conducted for the determination of the viscosity of air and when the results obtained (which will be published shortly elsewhere) agreed very well with the recent work of other investigators, it was thought desirable to apply the same method for the determination of the viscosity coefficients of the gases mentioned above, with a view to determine more accurate values of these constants.

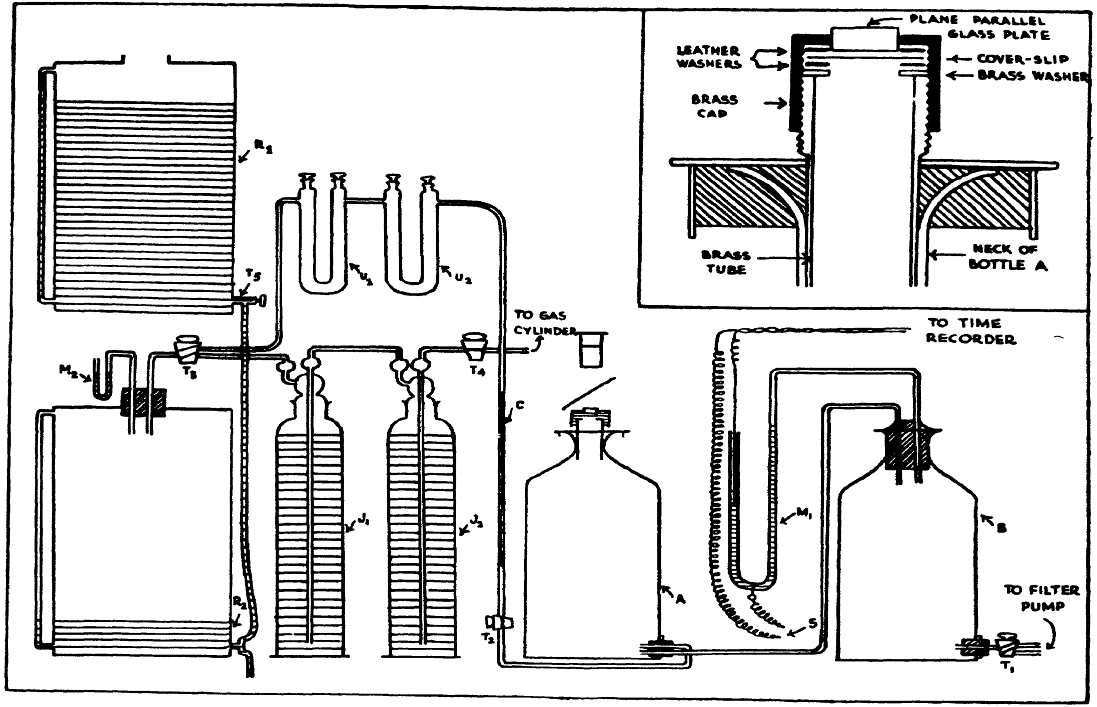
I. EXPERIMENTAL ARRANGEMENT AND GENERAL METHOD OF WORK.

The apparatus used in these experiments for measuring the viscosity of gases does not differ in principle from the one used by Wagstaff, but devices to dehydrate the gas and to measure automatically-the time during which the gas flows through a capillary tube have been added. An arrangement to keep the gas at constant (atmospheric) pressure has also been devised.

The general lay-out of the apparatus is shown in the figure and the inset shows details of the holder for the microscope cover-slip.

The apparatus may be said to consist of four parts, namely, (1) the exhaust chamber, (2) the reservoir of gas, (3) the dehydrating system for gases, and (4) the automatic device for measuring time intervals.

(1) *The Exhaust Chamber.*—Wolfes' bottles A and B form the exhaust chamber and their total volume is about 5000 c. c. In the mouth of the bottle A is placed the holder for clamping



GENERAL LAY-OUT OF THE APPARATUS

Inset shows the details of the cover-slip holder.

A B, Wolfe's Bottles; C. Capillary tube; J_1, J_2, Dehydrating (H_2SO_4) Jars; M_1, M_2 Manometers; R_2 Reservoir of Paraffin Oil; R_2 Reservoir of Gas; S Switch; T_1, T_2, T_3, T_4 Glass Taps; T_5 water-tap; U_1, U_2 $CaCl_2$ Tubes, the microscope cover-slip. It is a tightly fitting brass tube which is threaded at its upper end on its outer surface. On top of this tube is placed a thick copper plate with an aperture of radius O·79 cm. Due care was taken that the centre of the plate was on the axis of the tube. Over this plate a microscope cover-slip of thickness 0·0225 cm. was placed, and the latter was tightly clamped by screwing a brass-cap over the tube, This brass cap had an aperture of radius 0·79 cm. which coincided with the aperture of the plate. Thus an area of radius 0·79 cm. was acted on by the difference of pressure between that of the atmosphere and that within the exhaust chamber.

An optically plane circular plate of the same diameter as the exposed part of the cover slip was placed in the cap over the cover-slip. Newton's rings formed according to ordinary arrangements were observed by a microscope. Any change of pressure within the exhaust chamber changed the sag of the cover-slip and the number of Newton's rings that converged towards the çentre were counted, from which the change of pressure was calculated according to Wagstaff's formulla.

(2) *Reservoir of Gas*—R_1 and R_2, the reservoirs of liquid paraffin oil and gas respectively, are cylindrical copper vessels of about 6 litres capacity and tinned from the inside. As the gas in R_2 is at atmospheric pressure and that in the exhaust chamber is below that pressure, gas flows out from R_2 through U_1 and U_2 and the capillary tube, to the exhaust chamber. Thus, the pressure within R_2 should in the ordinary course decrease, but in this arrangement, paraffin oil flows from R_1 to R_2 and the gas remaining in the latter reservoir is compressed and the flow of paraffin is so adjusted (by means of the tap T_5) that the pressure remains nearly constant (atmospheric). The manometer M_2, which contains liquid paraffin, shows the change in pressure, if any, in R_2. The use of liquid paraffin, is preferable on account of its low coefficient of viscosity and also because its vapour pressure is negligible compared with other equally viscous liquids. It is interesting to find that Bond[2] has also used paraffin oil for the same reasons in his apparatus for determing the coefficient of viscosity of air, although it may be pointed out that this liquid was used even in the initial experiments (on air) the results of which were published by the authors[3] in September 1936.

(3) *The Dehydrating System for Gases:*—The gases are led to the apparatus through sulphuric acid in jars J_1 and J_2 and is stored in the vessel R_2. The gas is then led to the exhaust

chamber through the $CaCl_2$ tubes U_1 and U_2 and the capillary tube. Thus the gas passing through the capillary tube is dehydrated as far as is possible.

(4) *Automatic Device for Measuring Time Intervals*:—The manometer M_1 serves a double purpose—firstly, it shows the initial pressure to which the cover-slip is subjected and secondly, it serves to complete the electrical circuit which operates the time recorder. A platinum electrode is fused in the bend of the U-tube of the manometer, and a thick copper wire capable of sliding in one arm of the tube forms the other electrode. These electrodes, together with an accumulator, a pair of magnet-coils and a switch are all connected in series. The magnet-coils are from an electric bell, from which the make-and-break contacts are removed and the armature carries a sharp lead pencil which can press against a drum which rotates at a very steady rate by means of a clockwork. The pencil point draws a line on the paper wrapped around the drum, only when mercury in the manometer M_1 completes the electrical circuit. The magnet-coils are mounted on a carriage which can move horizontally on guide-rails. By means of a mechanical arrangement the carriage moves horizontally simultaneously as the chronometer drum revolves. Thus, the pencil point actually draws a spiral on the paper, and by previous calibration the length of the line gives the time interval during which the current was allowed to pass through the magnet coils.

The circumferance of the chronometer drum was exactly 50 cms. and it was made to revolve once in every 25 seconds. The latter was adjusted by means of an accurate stop-watch. The minimum distance that can be measured with accuracy by the unaided eye is one mm. and this is the length of the mark made by the pencil in 0·05 second. Hence the minimum time interval that could be measured was 0·05 second.

On an inspection of the general lay-out of the apparatus, it will be noticed that even if the switch S is closed, current will not be fed to the time recorder if mercury does not complete the electrical circuit between the platinum electrode and the thick copper electrode placed in the open limb of the manometer M_1. Thus the current is fed to the time recorder as soon as mercury rises to a predetermined height in the open limb of the manometer, which can be adjusted by moving the thick wire up or down, as required. Again, as soon as the coils are energised by the flow of current through them, a light tick is heard as the pencil point is pressed against the chronometer drum, which gives the signal to the observer to begin counting the rings which converge towards the centre, as seen through the microscope. Thus this arrangement is automatic because the time recorder is put into action as soon as a predetermined pressure is reached in the exhaust chamber and the observer has only to open the switch to break the electrical circuit, after a number of Newton's rings have converged to the centre, the time interval being marked on the paper.

After the apparatus had been set up, a special experiment was performed to determine Young's Modulus for glass of cover-slip using Wagstaff's formula, which is,

$$E = \frac{45}{128} \frac{R^4 p'}{t^3 N\lambda}$$

where "E" denotes Young's Modulus, "t" the thickness of the cover-slip, "R" the radius of the surface of the cover-slip subjected to pressure, "p′" being the change in pressure when "N" Newton's rings of wave-length "λ" converge towards the centre. The value of "E" for glass of the cover-slip used in these experiments was $5 \cdot 8 \times 10^{11}$ dynes per sq. cm.; this experiment gave the value of the ratio p'/N as being 0·2136 cm. of mercury per Newton's ring that is, if a Newton's ring converged towards the centre, the pressure changed by 0·2136 cm. of mercury.

When an observation was to be taken, the reservoir R_2 was first completely filled with paraffin oil and the reservoir R_1, which was empty, was placed at a lower level than the former. Paraffin oil is then made to flow from one of the tubes attached to the Y-shaped tube of the reservoir R_2 to the reservoir R_1. The glass tap T_4 is then opened to allow the passage of the gas from the cylinder, and as paraffin oil flowed out from the reservoir R_2 its place was taken by air. Thus when the cylinder contained no paraffin oil, it was full of dehydrated gas on which experiments were to be made.

The pressure in the exhaust chamber was then reduced by means of a filter pump and the relative heights of the mercury columns in the two limbs of the manometer M_1 were measured by means of a carefully adjusted cathetometer. The thick wire in the open limb of the manometer was then so adjusted that its point just touched the surface of the mercury column in that limb. With the adjustment of the initial pressure, the barometer as well as the thermometers were also read.

The flow of paraffin oil was so adjusted that the mean pressure during the experiment (in the reservoir R_2) remained at nearly the atmospheric pressure and also that the difference from this pressure was as small as possible. The tap T_5 was then left untouched and pinch-cock stopped the flow of paraffin.

The pressure within the exhaust chamber was then reduced to a value slightly less than the predetermined initial pressure to accustom the eye of the observer to the passage of Newton's rings and also to be ready to begin the count as soon as the initial preassure was reached.

The tap T_2 near the capillary tube was then opened, (the pinch-cock on the rubber tube connecting the two reservoirs having already been removed), gas flowed from R_2 to the exhaust chamber and the pressure within the latter increased, and Newton's rings were seen to converge towards the centre. As soon as the predetermined pressure was reached in the exhaust chamber, the time recorder came automatically into action.

After the required number of rings had converged towards the centre, the tap near the capillary tube was closed and the pinch-cock again applied to the rubber tube to stop the flow of paraffin oil. Of course, the electrical circuit had already been broken, by means of the switch S, when the last ring disappeared.

II. THE FORMULA USED IN CALCULATIONS

The formula used in the determination of the coefficient of viscosity is the same as that given by Wagstaff[1], namely,

$$\eta=\frac{\pi a^4\cdot T}{8\cdot l\cdot S}\cdot\frac{p_2}{\log_e\dfrac{(p_2+p_1+p'}{(p_2-p_1-p'}\cdot\dfrac{p_2-p_1)}{p_2+p_1)}}$$

where the gas of viscosity "η" flows through a capillary tube of length "l" and of radius "a", the total volume of the apparatus being "S"; the pressure difference at the two ends of the capillary tube is "p_2-p_1" initially, "p_2" being the atmospheric pressure, the gas having flowed for a time "T" during which the initial pressure has changed by an amount "p'", the latter being given by the formula on page 29.

The total volume of the apparatus, "S", was determined by filling the whole exhaust chamber from the tap T_1 to the tap T_2 with distilled water, and then measuring its volume.

The various constants for the apparatus used in these experiments were as follows :—

Thickness of cover-slip $\equiv t = 0\cdot0225$ cm.

Radius of aperture in cap of the cover-slip holder
$\equiv R = 0\cdot79$ cm.

Young's Modulus of glass of cover-slip (determined from experiment) $\equiv E = 5\cdot8 \times 10^{11}$ dynes per sq. cm,

Total volume of the apparatus $\equiv S = 5045$ c.c.

Capillary tubes of different lengths and bores were used (four different tubes).

III. RESULTS

In these experiments, the mean of three readings of the time interval for a given number of rings at a fixed initial pressure was used for calculations, and the value of the viscosity coefficients of the gases were determined from separate sets of readings corresponding to a particular temperature.

In the case of carbon di-oxide, the temperature correction formula suggested by Britenbach[4] was applied, namely,

$$\eta_{23^\circ C} = \eta_{\theta^\circ C} + 0\cdot000000477\ (23 - \theta),$$

where $\eta_{23^\circ C}$ is the value of the viscosity coefficient of CO_2 at 23°C, and $\eta_{\theta^\circ C}$ the value at θ°C.

A similar empirical formula for the temperature correction of the coefficient of viscosity of oxygen has been given by States[5] to be

$$\eta_{23^\circ C} = \eta_{\theta^\circ C} + 0\cdot000000554\ (23 - \theta).$$

For nitrogen, no empirical formula for temperature correction has yet been employed, but from the results of these experiments, the following formula seems to hold good between 27·7°C and 28·3°C :—

$$\eta_{23^\circ C} = \eta_{\theta^\circ C} + 0\cdot000000460\ (23 - \theta).$$

Carbon di-oxide and oxygen used in these experiments were commercially pure, and nitrogen was prepared in the laboratory used one of the methods given by Thrope[6], namely, the warming of a paste of 1 part $NaNO_2$, 2 parts $(NH_4)_2SO_4$ and 1 part $K_2Cr_2O_7$ (all parts by weight) and then washing the gas evolved with 5 volumes of $K_2Cr_2O_7$ and 1 volume of H_2SO_4.

A typical set of results obtained during an experiment is given in table I.

TABLE I.

Gas Used—CO_2.

Temperature—28·6°C.

p_2-p_1 cms. of Hg.	p_2 cms. or Hg.	p_1 cms. of Hg.	N	T secs.	$\eta\times10^{+4}$ c. g. s. units.
14·08	76·71	62·65	5	11·5	1·50492
			10	23·9	1·50550
			15	37·4	1·50729
			20	53·4	1·50818
			25	68·5	1·50755
			30	86·8	1·50697
			35	107·8	1·50804
			40	132·2	1·50734
			45	161·0	1·50659
			50	250·0	1·50409

Mean Valus of $\eta_{28\cdot6^\circ C}=1506\cdot65\times10^{-7}$ c. g. s. units.

Calculated Value $\eta_{23^\circ C}=1479\cdot97\times10^{-7}$ c. g. s. units.

Tables II, III and IV give the summaries of the results obtained using carbon di-oxide, oxygen and nitrogen rerpectively, (constants of the capillary tube used were $a=0\cdot02378$ cm., and $l=22\cdot45$ cms).

TABLE II.

Carbon di-oxide.

Temperature θ °C ·	$\eta_{\theta^\circ C}\times10^7$ c. g. s. units.	$\eta_{23^\circ C}\times10^7$ c. g. s. units.
29·4	1510·37	1479·84
29·0	1508·37	1479·75
29·4	1510·82	1480·29
29·2	1509·34	1479·77
29·4	1510·21	1479·68
28·6	1506·65	1479·97
29·4	1510·25	1479·72
29·0	1508·26	1479·64
29·4	1510·65	1480·12
29·0	1508·03	1479·41
29·6	1511·76	1480·28
29·2	1509·99	1480·42

The mean value of the viscosity coefficient of carbon di-oxide (from 100 independent observations) is $\eta_{23^\circ C}=(1479\cdot9\pm0\cdot5)\times10^{-7}$ c. g. s. units.

TABLE III.

Oxygen.

Temperature θ°C	$\eta_{\theta^\circ C}\times 10^7$ c.g.s. units	$\eta_{23^\circ C}\times 10^7$ c.g.s. units
27·0	2060·44	2038·98
27·4	2062·64	2038·36
27·4	2062·69	2038·31
27·4	2062·57	2038·19
27·4	2062·89	2038·51
27·4	2062·82	2038·44
27·6	2063·79	2038·31
27·8	2064·71	2038·11
27·4	2062·68	2038·30
27·4	2062·61	2038·24
27·4	2062·94	2038·56

The mean of 90 independent observations gives the value $\eta_{23^\circ C}=(2038\cdot33\pm0\cdot56)\times10^{-7}$ c.g.s. units.

TABLE IV.

Nitrogen.

Temperature θ°C	$\eta_{\theta^\circ C}\times 10^7$ c.g.s. units	$\eta_{23^\circ C}\times 10^7$ c.g.s. units
27·7	1789·77	1768·15
27·7	1789·20	1767·58
27·7	1789·37	1767·75
28·2	1791·76	1767·84
28·2	1791·32	1767·40
28·2	1792·04	1768 12
28·3	1792·46	1768·08
28·3	1792·30	1767·92
28·2	1791·46	1767·54
28·2	1791·67	1767·75
28·2	1792·03	1768·01

In the case of nitrogen, the mean of about 90 independent observations, gave the value $\eta_{23^\circ C}=(1767\cdot83\pm0\cdot37)\times10^{-7}$ c.g.s. units.

This method has an advantage over the older mothods due to Rankine and others in that, there is no mercury pellet which acts as the driving force for the gas under experiment. The capillary tube in the experiments described above was connected by wide rubber tubes to the rest of the apparatus as against fusing of the capillary tube to wider bore tubes in Rankine's apparatus. Thus no corrections of the nature involved in the apparatus of Rankine and others were necessary.

In other methods for measuring the coefficient of viscosity of a gas, the relative heights of mercury columns give the pressure reading and two such readings had to be taken to know the pressure difference which a certain quantity of gas caused by virtue of its flow through the capillary tube in a certain interval of time. But in this method, the pressure change is indicated, by the convergence of interference rings towards the centre, at the same time that the gas is flowing; moreover due to the automatic arrangement for recording time, the personal factor has to a large extent been reduced, the observer having only to count the number of Newton's rings which converge towards the centre.

The authors have to express their sincere thanks to Professor G. R. Paranjpe, Head of the Department of Physics, Royal Institute of Science, Bombay, for the valuable suggestions given by him during the course of the experiments and also for the keen interest shown by him in the work.

Thanks are also due to Dr. T. S. Wheeler, Principal, Royal Institute of Science, Bombay, for giving us all facilities to carry out this work.

SUMMARY

Using a modified form of Wagstaff's[1] apparatus for measuring the coefficient of viscosity of gases by the method of interference fringes and using capillary tubes, the following results have been obtained:—

For Carbon di-oxide, $\eta_{23^\circ C}=(1479\cdot 9\pm 0\cdot 5)\times 10^{-7}$ c. g. s. units.

For oxygen, $\eta_{23^\circ C}=(2038\cdot 33\pm 0\cdot 56)\times 10^{-7}$ c. g. s. units.

For nitrogen, $\eta_{23^\circ C}=(1767\cdot 83\pm 0\cdot 37\times)10^{-7}$ c. g. s. units.

A temperature correction formula for nitrogen (obtained from the results of these investigations) in the form

$$\eta_{23^\circ C}=\eta_{\theta^\circ C}+0\cdot 000000460(23-\theta).$$

also seems to hold good.

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1. Wagstaff, *Phil Mag.*, 1923, *45*, 84.
2. Bond, *Proc. Phys. Soc.*, 1937, *49*, 205.
3. Majumdar & Vajifdar, *Current Science*, 1936, *5*, 133.
4. Britenbach, *Ann. d. Physik*, 1901, *5*, 166.
5. States, *Phys. Rev.*, 1923, *21*, 662.
6. Thorpe, *Dictonary of Applied Chemistry*, Vol. IV, 542, (1922 Ed.)

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INVESTIGATION OF SMOKE POLLUTION IN AHMEDABAD, NOVEMBER 1937

By

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The present investigation is made on similar lines to the Bombay one[1]. The actual number of solid smoke and dust particles in one cubic centimeter of air has been found at various centres and on two different days. The samples of air were collected in specially designed aspirator flasks. A rubber baloon was fully blown into the flasks thus displacing all the air it originally contained. The balloon was then allowed to be deflated and consequently fresh smoke-bearing air from the particular centre entered the flask. A small known volume of air from this sample was sucked into an expansion chamber, containing some water. The air in the expansion chamber was then suddenly expanded. This resulted in the formation of a cloud of water drops. Originally the expansion chamber was free from any dust or smoke particles and hence a cloud could not be formed by a low expansion. It is only when there are dust or smoke particles that a cloud is formed. Each particles serves as a centre of condensation of water. The total quantity of water condensed can be calculated by knowing the expansion. The size of the drops can be determind by observing the radius of a corona ring seen in a cloud by looking through it at a distance source of light. By knowing the above factors, the number of particles per cubic centimeter can be estimated.[2]

The days selected for taking measuraments were the 4th and 7th November. All the mills remained closed on the 3rd, 4th and 5th, being Diwali holidays. The 4th November was chosen with a view to find out the impurities in air due to causes other than mill smoke. The mills began work on the 6th November and hence the following day was quite suitable to find the total

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(1) "Pollution of Bombay air by Smoke" Bom. Univ. Jour. 66, 3 pt. II., 1934.

(2) "A new method of estimating the number of dust particles in air," Bom. Univ. Jour. 58, 3 pt. II, 1934.

pollution on a woking day. Six different centres were chosen, out of which four were selected in the busy mill area and two were selected outside the city limits and mill area. The results are tabulated below. The number in each column indicates the number of particles per cubic centimeter.

Centres.		November 4th Evening 7 to 8 P.M.	November 7th Morning 9 to 10 A.M.	November 7th Evening 8 to 9 P.M.
		number of particles per cubic centimeter		
(1)	Naroda Road ...	2540	6450	14690
(2)	Gomatipur ...	2360	8630	13720
(3)	Bhadra ...	4330	8840	14160
(4)	Kalupur ...	2770	9130	15080
(5)	Gujrat College ...	2940	3540	9300
(6)	Shahibag ...	1455	3450	6158
	Average from 1–4..	3000	8440	14158

The first column of the results are of special importance as they were taken on a day when no smoke from the mills could be expected to be present in the atmosphere. Whatever amount of smoke or dust that was observed on that day must therefore be attributed to smoke from domestic fire and dust due to traffic or wind. A place like Bhadra is of special interest. One finds a a maximum pollution here as the traffic is the heaviest at this place. The Kalupur centre is also in a busy traffic locality and thus stands second highest. The difference in the Bhadra and the Kalupur results may be partly due to the smoke from Diwali crackers, which were more prominent in the Bhadra Locality. Gomatipur and Naroda road, though thickly surrounded by mills, show less pollution on account of less traffic. The place near Gujrat College also indicates a fairly high pollution. This must be due to the smoke from the city that diffused in that direction by a low wind, which appeared to blow at about 5 miles per hour. The Shahibag area shows the least pollution, being situated outside the city limits and in a direction towards which the wind was not blowing from the city.

I. It is evident from the above results that on an average the pollution of Ahmedabad air by smoke and traffic dust is of about 3000 particles per c. c.

The investigations of Bombay air in 1934 indicated that 1200 particles per c. c. may be due to particle other than of mill smoke. The average Sunday evening result indicates a pollution of about 2500 particles per c. c. Thus the pollution in Bombay due to dust and domestic fire can be taken to be about 2000 particles per c. c.

II. The air in Ahmedabad, therefore, contains about 1000 particles more per c. c. of domestic smoke and traffic dust than in Bombay.

The results of the third Column, which were taken in the morning on the 7th, indicates an average pollution in the city of about 8440 particles per. c.c. The average smoke pollution outside the city limits is of about 3500 particles per cc. If we subtract 3000 particles other than of mill smoke, we get a pollution of about 5440 particles per c.c. of smoke-particles from mills in the morning. The average morning nuisance in Bombay is about 2440 particles per c.c. of which about 1200 particles other than of mill smoke. Hence in Bombay the number of smoke particles from mills is about 1200 per c.c.

III One concludes from the above that in Ahmedabad there are about 8440 particles per c.c. in the air in the morning, of which about 5440 particles are due to mill smoke alone.

IV The pollution of Ahmedabad air by mill smok in the morning is about 4·5 (=5440/1200) times more than in Bombay.

One finds a considerable increase in the evening pollution of air. The smoke emitted by the mill chimneys during the course of the whole day slowly descends downwards and is responsible for the increase of the pollution. The average pollution in the city proper is of about 14400 particles per c.c. The average pollution outside the city areas is of about 7500 particles per c.c. Assuming again that about 3000 particles are due to other causes than the mills, we find about 11400 particles of mill smoke from mills in the evening. In Bombay the average number of particles in the evening is about 3600 per c.c. of which about 1200 are of other than mill smoke; hence 2400 particles per c.c. are from mills alone.

V It is therefore evident that there are over 14000 particles per c.c. in the Ahmedabad air in the evening, of which about 11000 particles are of mill smoke only.

VI The evening pollution of the Ahmedabad air by mill smoke alone is 4·7 (=11400/2400) times that in Bombay.

It is seen from IV and VI that the ratio of contents of the mill smoke in Ahmedabad to Bombay is about 4·6.

My thanks are due to the authorities of the Royal Institute of Science for allowing me to take a large number of apparatus to Ahmedabad and giving me the necessary permission to carry out this investigation. Thanks are also due to the Smoke Nuisances Commission for granting me permission to publish these results.

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THE VISCOSITY OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES

By

J. D. RANADE AND G. R. PARANJPE

Since 1929, considerable amount of work on viscosity of electrolytes has been done at very low concentrations by Jones and Talley[1], Wolfendon in conjunction with Joy and Cox[2],[3] and others. But all this work was done at temperatures 35 °C or less. Only Sulston[4], has worked above this temperature.

So it was thought useful to obtain experimental data and apply the same to the equation suggested by Falkenhagen[12] at temperature higher than 35°C. Again, the temperature 35°C was particularly chosen as the working temperature as it was thought that it would provide a check on this work and would enable a comparison with data previously available. There was some interest as to the nature of the relation between the coefficients A and B of the Jones and Dole[6] equation and the temperature.

The present work was undertaken with a view to study the relationship of the concentration with the viscosity at temperatures higher than 35°C and of salts which are highly hydrated and hence cause complexities due to the thermal decomposition of hydrates.

Rajderkar and Paranjpe[5], had studied about 8 chlorides at temperatures above 35°C and they had chosen concentrations from 0.25 N to 1N. Jones and Dole[6], equation was just published at that time and attempts were made to apply this to the solutions investigated then. But they were more concentrated than the theory had contemplated. Thus the present work forms a continuation of the former work in as much as nearly the same salts are chosen but the concentrations worked upon are lower, ranging from ·1 molal to ·01 molal.

On the assumption that a common ion would facilitate comparison, the electrolytes chosen are all chlorides. Some are monovalent and some divalent. The solvent was water in all cases. Another reason for the choice of these salts is that some of them, for instance KCl, NH_4Cl are known to exhibit the so-called negative viscosity. There was also another point of interest. Jones and Dole[6], had predicted and verified that even the salt which shows diminished viscosity at moderate concentrations and low temperatures may show viscosity greater than water at very low *concentrations*. Joy and Wolfendon[8], tested this prediction by a new data on KCl, $RbNO_3$, $KClO_3$, and HNO_3, at 18°C and 35°C. They found that HNO_3 increases the viscosity at all concentrations at both of these temperatures and KCl and $KCLO_3$ behave likewise at 35°C. So KCl and NH_4Cl were selected to see whether they showed increased viscosity at temperatures higher than 35°C.

EXPERIMENTAL

Appleby[7], has showed that the values of absolute viscosity of water, determined by accurate methods, diverge from each other from 0·3 to sometimes 1·0%. But viscosity of aqueous solutions of salts relative to that of water can be measured with a precision of 0·01%. Relative measurements are usually more precise due to the simplified form of the apparatus used. Errors in measuring the length and the radius of the capillary and also errors due to the end conditions of the capillary are inevitable but they can be avoided or at least minimised. Water was taken as the standard substance. The viscosity and density of water at different temperatures are accurately known and the viscosities of solutions (mainly dilute) do not differ much from that of water at different temperatures.

Apparatus.

The apparatus is shown in Fig. 1 in side and front elevation. It consists of a capillary flow Ostwald type of viscometer AB made entirely of quartz, and enclosed in an air thermostat provided with a large glass window, XY, for observation. The end B is connected through a two way tap S to the filter-pump through the safety bottle P, or alternatively to the air in the thermostat by means of the tubing N. Initially the liquid in the large reservoir A is drawn up into the small reservoir B by operating the filter-pump connected to it through the tap S. By turning the tap S the other way, it is then connected with the air in the thermostat. The time of fall of the meniscus between two marks on the bulb B is noted by a stop-watch, the transits past the marks being observed through a cathetometer. The apparatus is well illuminated from outside by the light bulb C.

Viscometer and Viscometry.

A Viscometer, according to the suggestions of Washburn and Williams[8], made entirely of quartz, and specially ordered for the investigation was used. The type was according to that suggested by Grinnel Jones and S. K. Talley[1].

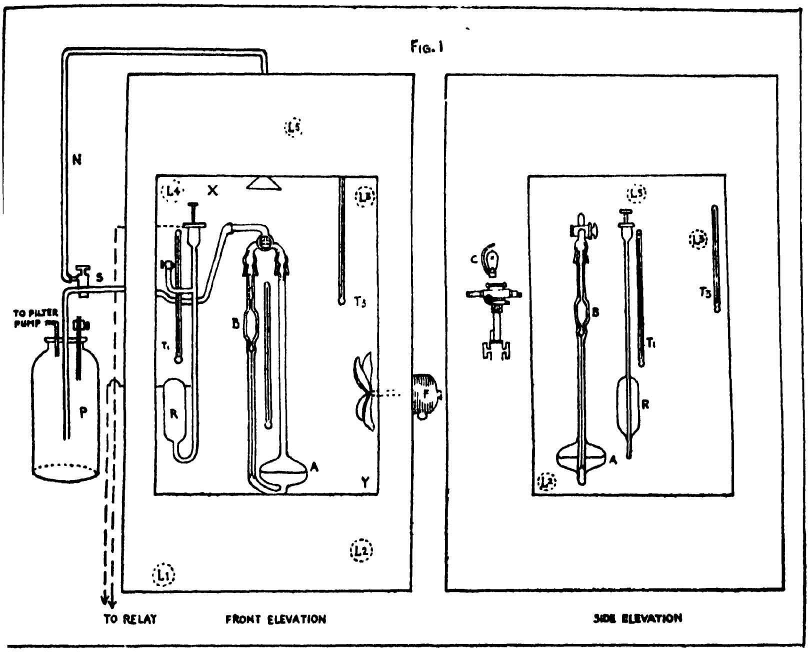


Fig. 1

The viscometer is shown in Fig. 1. There is a large reservoir A with a bent end at the bottom which becomes narrow gradually. This is connected with a smaller bulb B by the capillary which is vertical. They form two limbs of the viscometer, the general appearance being U shaped. There is a removable RS' provided with a three way stop-cock K and a right angled bent tube L which is to be connected to the filter-pump. When the stop-cock K is in either of the vertical positions the tube L is connected with that side of the viscometer, but when it is kept horizontal the two limbs are connected with each other. Near the bulb B, there are two constrictions C_1 and C_2 on which two marks are made. This avoids surface tension effects.

Quartz has a very small co-efficient of expansion and hence the dimensions of the instrument do not vary appreciably with temperature. Also there is no solvent action of water or other cleaning reagents on it. Many other errors like the presence of solid particles, blocking the capillary, temperature hysterisis, contamination of water by dissolved gases, are avoided or greatly minimised. The Ostwald type construction is also helpful in minimising drainage or surface tension effects.

Some of the important dimensions are as given below:—

Average hydrostatic head = 22·8 cm.
Volume of bulb B = 10·06 c. c.
Length of the capillary = 18·5 cm.
Diameter of the capillary = ·0476 cm.

Since in these experiments, only the hydrostatic pressure caused by the difference in levels in the two bulbs is used, all the complications of external pressure arrangements, the air-tight joints and exact measurements by a manometer are completely eliminated.

The accuracy of the work depends upon keeping the instrument always in a fixed and definite position. The viscometer was always kept in a base (wooden) specially prepared so as to hold the large bulb A firmly. It was permanently fixed by screws to the thermostat box and this completely avoided any shift in the lateral direction. The limbs were clamped firmly to fixed iron stands forming a rigid frame. It is important that after the instrument is removed from the thermostat for cleaning and refilling, it should always be put back in a definite reproducible position so that the hydrostatic head remains constant As there was no external pressure used and the pressure head was not much, the kinetic energy correction was very much reduced. Moreover the time of flow was sufficiently long so as to make the correction vanishingly small.

The arrangement for temperature control was a thermostat and nearly the same as described by Rajderkar and Paranjpe.[5] The temperature could be maintained within ±0·05°C for continuous working of six to seven hours.

After cleaning, drying and filling the viscometer, it was kept in the thermostat for about half an hour in order that it should attain the temperature of the enclosure. The disturbances caused by movement of and pouring in of the liquid etc also disappear in this time. By turning the three-way cook K in the pyrex cross-piece, the small bulb B was connected with the filter-pump. Liquid was sucked in the bulb and when the leval was somewhat above the transit mark, the limbs were put in connection with the air in the thermostat. A cathetometer was focussed on two definite marks on the small constrictions C_1 and C_2 and the time of flow between these two levels was recorded. The liquid was sucked up and allowed to fall without noting the time at least thrice as the time required just in the beginning is usually a little higher than the successive readings due to unsettled conditions.

Precautions taken to avoid evaporation of the liquid or condensation due to rushing in of cold air from outside :—

This was avoided by connecting the tube N to the inside of the thermostat chamber. Also, the possibility of evaporation due to high temperatures and consequent changes in the concentration of solutions was avoided by connecting the viscometer to the filter-pump through a bottle P containing water and hence the air above the solution was saturated with the vapour from the solution.

Density of solutions enters into the calculation of the relative viscosity as a direct factor and therefore needs to be known with the same precision as the time of flow. For this reason the densities were measured by means of large specific gravity bottles the relative viscosity of the solution is given by

$$\frac{\eta_e}{\eta_w} = \frac{d_e}{d_w} \cdot \frac{t_e}{t_w} \text{ where}$$

η_e. η_w ; d_e d_w, and t_e t_w are respectively the coefficient of viscosity, density and time of flow of the electrolytic solution and distilled water, provided, of course, the same hydrostatic pressure is always used (Hatschek[14].) η_e thus becomes the absolute and η_e/η_w the relative coefficient of viscosity of the solution.

K. E. correction is not applied as a well designed instrument having dimensions as suggested by Gruneisen[9] does not deviate from Poiseuille's law. Mereover Applebey[7] has put it in his reply to the criticism on his work by Bingham[10]. "A systematic study of the Ostwald viscometer shows that the deviations are not due to K. E. lost but due to eddy formations at the points where there is a rapid change of flow and moreover the corrections as suggested by Hangenbach, Wilberforce etc. are meant for instruments where the exit of liquid opens into air but not for instruments like Ostwald type where the capillary opens in a reservoir of the same liquid". Bingham also admits that the correction is negligible if the times of flow are long, η and η' are not differing much and the solutions worked upon are dilute as is the case in the present work.

The water used both for making up the solutions and to determine the period of the viscometer was double distilled water. All salts used, were those supplied by E. Merck, extra-pure type, accepted to have contained no impurities in sufficient amounts to affect the results measurably, Measurements of the co efficient of viscosity at three temperatures between 30° and 60° were made on the following salts :—

1. Lithium chloride
2. Sodium chloride
3. Potassium chloride
4. Calcium chloride
5. Ammonium chloride
6. Barium chloride.

With each salt at least 8 to 10 concentrations ranging from 0.1 mol. to 0.01 mol. were studied.

The accompanying tables from I to VI contain the results. There are three tables for each salt, corresponding to the three temperatures at which measurements were made. The temperatures chosen are 35°, 45°, 55° the precise value of the temperature for a particular set of observations is given at the top of each table

TABLE I

C=*Concentration* (*Molal*) : *first column*

Relative Viscosity : *second column*

η_e=*Absolute Viscosity* : *third column*

AMMONIUM CHLORIDE

t=44·9°C			t=54·5°C		
C.	Relative viscosity	Absolute viscosity	C.	Relative viscosity	Absolute viscosity
0·101	1·0037	0·006041	0·101	1·0075	0·005148
0·070	1·0027	0·006036	0·081	1·0057	0·005138
0·061	1·0024	0·006034	0·070	1·0051	0·005135
0·050	1·0019	0·006031	0·061	1·0042	0 005131
0·041	1·0018	0·006030	0·052	1·0036	0·005128
0·032	1·0011	0·006027	0·041	1·0030	0·005130
			0·021	1·0019	0·005120
			0·010	1·0011	0·005115

TABLE II

BARIUM CHLORIDE

$t=35\cdot1$°C			$t=45\cdot0$°C			$t=54\cdot5$°C.		
C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity
0·101	1·0295	0·00745	0·100	1·0264	0·00617	0·100	1·0225	0·00522
0·081	1·0234	0·00741	0·091	1·0217	0·00615	0·091	1·0198	0·00521
0·072	1·0208	0·00739	0·082	1·0197	0·00614	0·080	1·0176	0·00520
0·061	1·0173	0·00737	0·070	1·0187	0·00613	0·061	1·0125	0·00517
0·052	1·0161	0·00736	0·060	1·0168	0·00612	0·052	1·0084	0·00516
0·040	1·0128	0·00733	0·051	1·0127	0·00609	0·030	1·0067	0·00514
0·031	1·0105	0·00732	0·041	1·0108	0·00608	0·021	1·C038	0·00513
0·020	1·0067	0·00729	0·030	1·0097	0·00607	0·010	1·0021	0·00512
0·010	1·0054	0·00728	0·021	1·0061	0·00605			
			0·010	1·0035	000·604			

TABLE III

CALCIUM CHLORIDE

$t=35\cdot6$°C			$t=45\cdot2$°C.			$t=54\cdot6$°C.		
C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity
0·087	1·0244	0·00742	0·070	1·0259	0·00617	0·088	1·0319	0·00527
0·070	1·0211	0·00739	0·062	1·0234	0·00616	0·070	1·0286	0·00526
0·062	1·0188	0·00737	0·053	1·0213	0·00615	0·062	1·0264	0·00524
0·053	1·0154	0·00735	0·044	1·0182	0·00613	0·053	1·0213	0·00522
0·035	1·0097	0·00731	0·035	1·0152	0·00611	0·044	1·0198	0·00521
0·013	1·0043	0·00727	0·026	1·0110	0·00608	0·035	1·0179	0·00520
0·008	1·0030	0·00726	0·013	1·0062	0·00606	0·026	1·0152	0·00519
			0·008	1·0051	0·00605	0·013	1·0111	0·00517
						0·008	1·0078	0·00515

TABLE IV

LITHIUM CHLORIDE.

$t=35\cdot5°C.$			$t=45\cdot3°C.$			$t=54\cdot9°C.$		
C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity
0·319	1·0424	0·00754	0·318	1·0416	0·00627	0·318	1·0394	0·00531
0·159	1·0163	0·00736	0·159	1·0123	0·00609	0·102	1·0045	0·005133
0·102	1·0118	0·00733	0·102	1·0076	0·00606	0·079	1·0030	0·005125
0·079	1·0077	0·00729	0·079	1·0050	0·00605	0·064	1·0022	0·00512
0·032	1·0045	0·00727	0·064	1·0028	0·00604	0·032	1·0011	3·00511
0·019	1·0021	0·00726	0·032	1·0019	0·00603	0·019	1·0006	0·00510
0·016	1·0020	0·00725	0·019	1·0015	0·00602			

TABLE V

POTASSIUM CHLORIDE

$t=35\cdot0$°C			$t=45\cdot0$°C			$t=55\cdot0$°C		
C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity
0·265	1·0082	0·00729	0·398	1·0139	0·00610	0·398	1·0145	0·00518
0·199	1·0056	0·00728	0·199	1·0086	0·00607	0·199	1·0092	0·00515
0·099	1·0034	0·00726	0·099	1·0048	0·00605	0·099	1·0047	0·06513
0·049	1·0024	0·007257	0·049	1·0028	0·00604	0·033	1·0018	0·00512
0·033	1·0019	0·007254	0·033	1·0022	0·006033	0·019	1·0011	0·005115
0·025	1·0011	0·007248	0·019	1·0015	0·00603	0·014	1·0009	0·00511
0·020	1·0009	0·007240	0·014	1·0008	0·006025			

TABLE VI

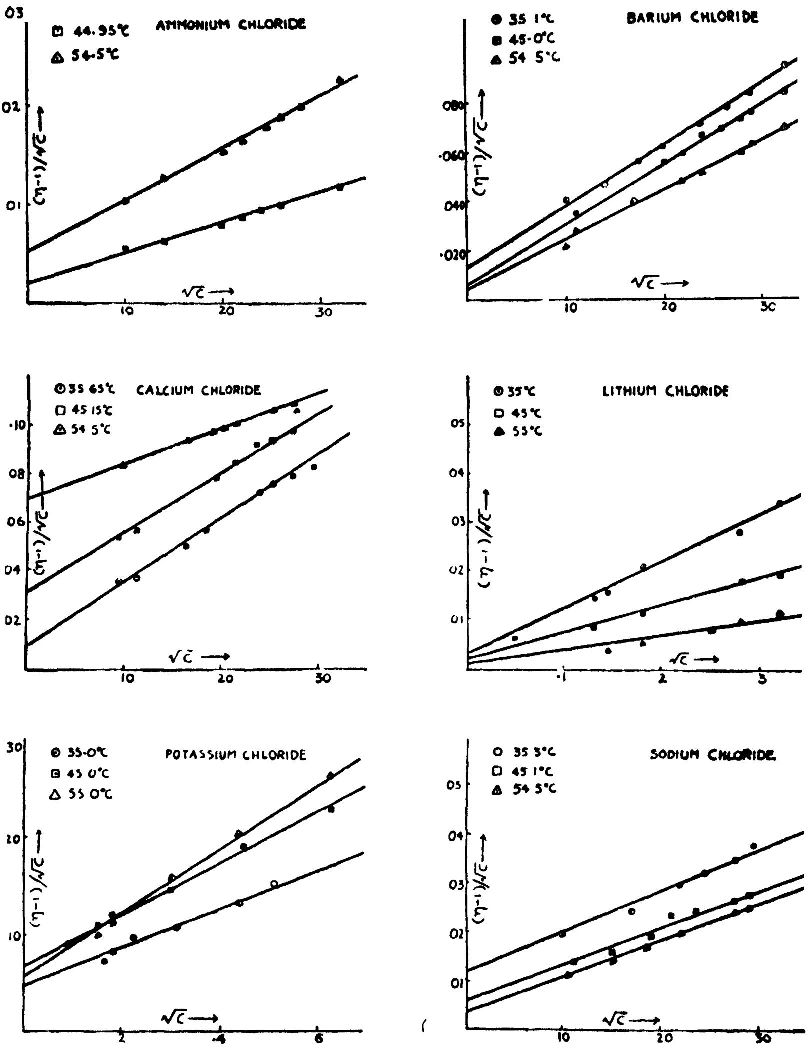
SODIUM CHLORIDE

$t=35\cdot2°C$			$t=45\cdot1°C$			$t=54\cdot5°C$		
C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity	C	Relative viscosity	Absolute viscosity
0·091	1·0117	0·00732	0·089	1·0120	0·00609	0·141	1·0139	0·00518
0·082	1·0104	0·00731	0·074	1·0087	0·00607	0·083	1·0104	0·00516
0·061	1·0084	0·00730	0·056	1·0058	0·006054	0·074	1·0082	0·00515
0·050	1·0068	0·00728	0·045	1·0051	0·006050	0·045	1·0046	0·005133
0·032	1·0043	0·00727	0·035	1·0036	0·00604	0·034	1·0033	0·005126
0·011	1·0020	0·00726	0·025	1·0022	0·00603	0·024	1·0021	0·005120
			0·013	1·0010	0·006025	0·011	1·0010	0·005115

DISCUSSION AND INTERPRETATION OF RESULTS.

The results are shown in figures 2 to 7 with concentration in mols per litre as abscissa and relative viscosity as ordinate.

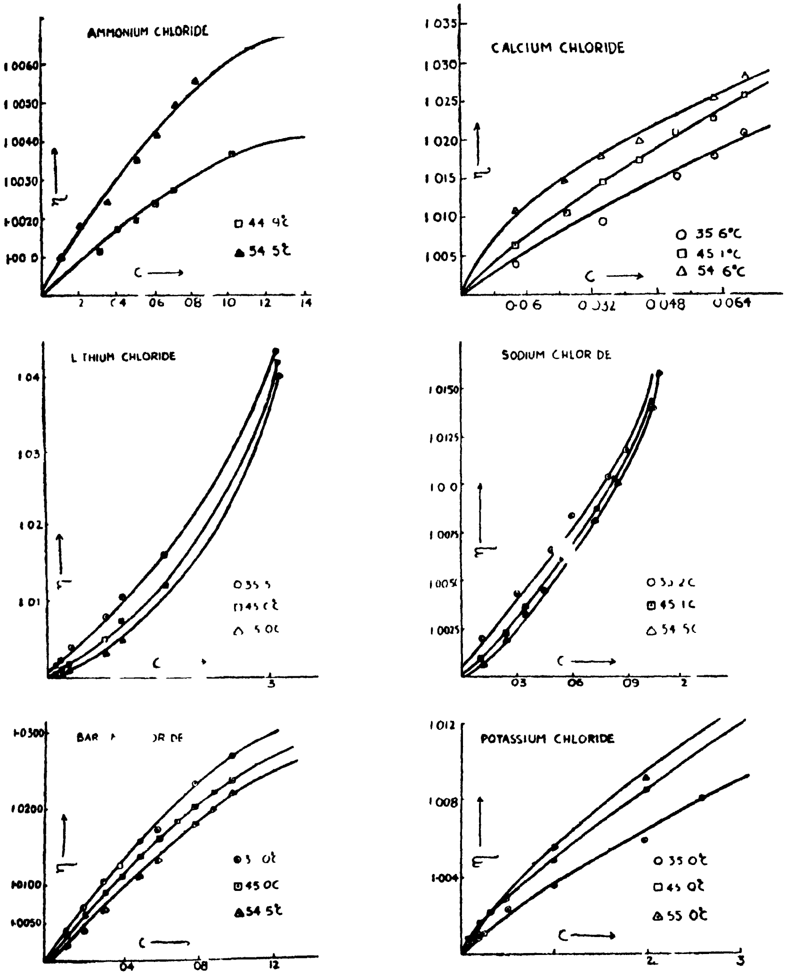
Figure 2—7



The equation (of Jones & Dole) $\eta=1+A\sqrt{c}\pm Bc$. may be readily transformed into $(\eta-1)/\sqrt{c}=A\pm B\sqrt{c}$. This equation may therefore be most conveniently tested by plotting $(\eta-1)/\sqrt{c}$

against $\sqrt{c}$
the vertical axis

Figure 8—13

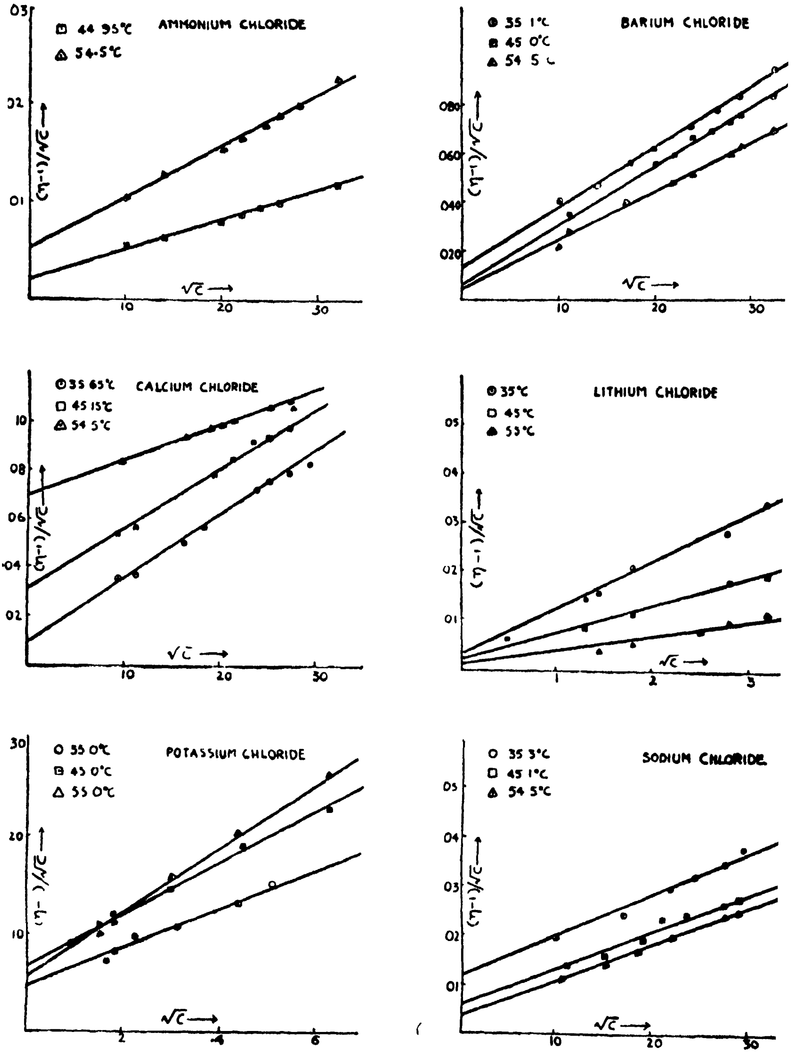


The experimental values of A and B computed by the method of least squares from the data above, to fit the Jones and Dole equation are shown in the following table No. VII and these values are compared with the theoretical values of A computed by the Falkenhagen and Vernon[15] equation.

DISCUSSION AND INTERPRETATION OF RESULTS.

The results are shown in figures 2 to 7 with concentration in mols per litre as abscissa and relative viscosity as ordinate.

Figure 2—7



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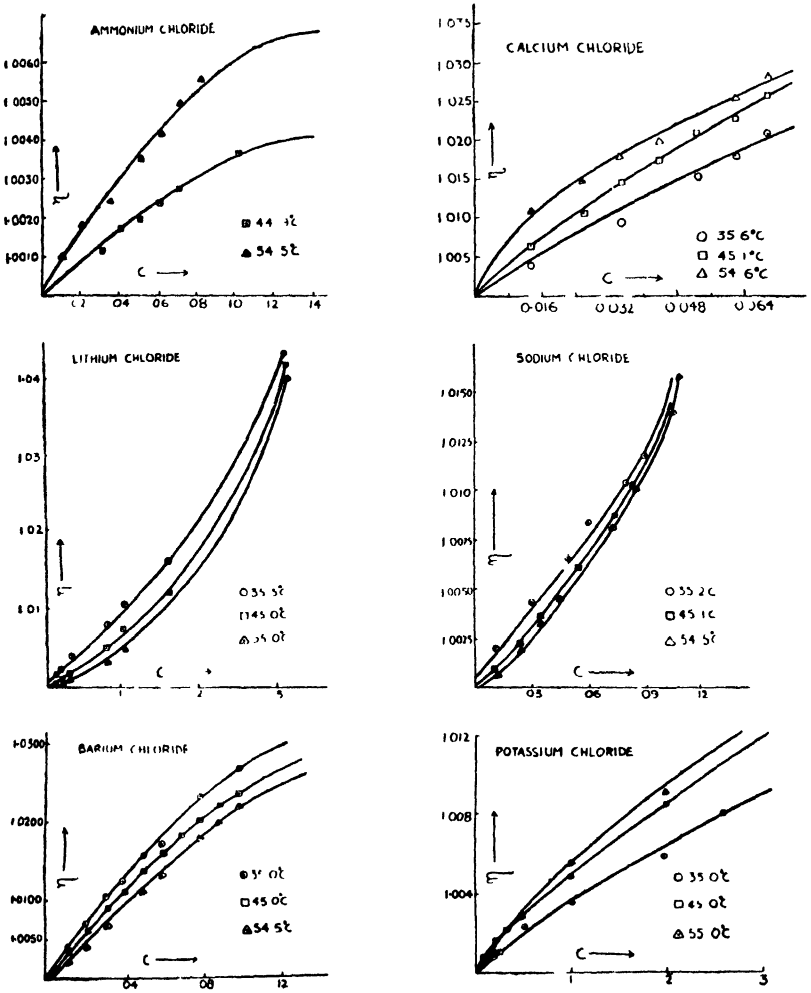
against $\sqrt{c}$ which should give a straight line whose intercept on the vertical axis is A and whose slope is B. (Figs. 8—13)

Figure 8—13



The experimental values of A and B computed by the method of least squares from the data above, to fit the Jones and Dole equation are shown in the following table No. VII and these values are compared with the theoretical values of A computed by the Falkenhagen and Vernon[15] equation.

TABLE VII

Values of the coefficients A and B in the Jones and Dole equations as calculated from experimental observations.

Salt.	Temperature in °c	Value of A (calculated)	Value of B (calculated)	Theoretical value of A according to Falkenhagen wherever available.
KCl.	0	...	...	0·0045
	18	...	...	0·0049
	25	...	...	0·0050
	* 35	0·0054	0·0197	0·0052
	45	0·0069	0·0244	...
	† 55	0·0057	0·0353	0·0055
NH_4Cl	25	...	...	0·0050
	45	0·0039	0·0241	...
	54·5	0·0057	0·0505	...
LiCl	0	...	...	0·0064
	18	...	...	0·0067
	25	...	...	0·0067
	35	0·0048	0·0926	...
	45	0·0010	0·0555	...
	55	0·0025	0·0534	...
NaCl	0	...	...	0·0056
	25	...	...	0·0060
	35	0·0103	0·0944	...
	45	0·0050	0·0984	...
	54·5	0·0035	0·0916	...

* Value of A by Sulston at 35°C.........0·0051
Value of A by Wolfendon and Joy at 35°C.........0·0051
† Value of A by Sulston at 55°C.........0·0041.

TABLE VII—*(concld.)*

Salt	Temperature in °c	Value of A (calculated)	Value of B (calculated)	Theoretical value of A according to Falkenhagen wherever available
$BaCl_2$	0	......	......	0·0138
	18	......	......	0·0145
	25	......	......	0·0147
	35	0·0114	0·2363	......
	45	0·0048	0·2453	......
	54·5	0·0055	0·1950	......
$CaCl_2$	35·6	0·0100	0·2400	......
	45	0·0338	0·2244	......
	54·5	0·0693	0·1474	......

In view of the difficulties of the work at the higher temperatures the observed values of A cannot be relied upon to more than ± 0·0015.

THE COEFFICIENT A

From the table No. VII it will be seen that the agreement between available theoretical values and the experimental ones is quite good for KCl for all temperatures. The agreement in values of KCl obtained and those given by other workers at 35°C and 55°C is noteworthy. While the value given by Sulston differs from the theoretical one at 55°C, the value given in this work is in better agreement with the theoretical one. The agreement is good for all the salts for the temperature 35°C. The theoretical values at 35°C being not available, those at the nearest available, temperature, that is 25°C, are given and it is seen that they compare quite well. For higher temperatures the values seem rather low compared to those at 35°C and it may be said that at higher temperatures the agreement would not be quite satisfactory.

It is evident from the formula of Falkenhagen[18] that the value of A depends in a very complicated manner upon the dielectric constant, viscosity of the solvent, the mobilities of the the solvent, the mobilities of the ions and in addition to these it varies inversely as the square root of the absolute temperature. There is probably some inaccuracy due to experimental difficulties in measuring mobilities. Most important from theoretical point of view is the fact that the variation of D, the dielectric constant with temperature is not thoroughly known. Falkenhagen says "It is probably impossible to state the change of A with temperature within an error of ± 15% because $\frac{dD}{dT}$ is not known accurately within ± 25%.

In the present observations the variation is the value of A with temperature is in the positive direction or there is a positive temperature coefficient in the case of the salts KCl and NH_4Cl, and $CaCl_2$ while in the case of LiCl, NaCl, and $BaCl_2$ the variation is in the opposite direction. Falkenhagen[18] while commenting upon the variation of A in the positive direction for some salte has given the view "There is no apparent reason why this order *i.e.* variation in a particular way, should hold for all electrolytes.". No mathematically worked out evidence is also available stating variation in a particular way. Sulston[4] has got positive coeffiicients for KCl and $MgSO_4$ but he has commented that it cannot be said whether the same thing will be true for other salts.

Now the discrepancy in the agreement at high temperatures is particularly observable in the case of highly hydrated salts like LiCl and others.

Whenever there is a discrepancy particularly at high temperatures, it may be presumably associated with higher terms of the ionic atmosphere function. The constant A was introduced by Jones and Dole to account for the inter-ionic forces and the resistance offered by the specially formed ionic lattice, to forces deforming it and the same view was taken while calculating the value for A mathematically. It is mainly introduced to explain the effect of inter-ionic forces on viscosity.

THE COEFFICIENT B.

Neither the absolute value of the constant B nor its variation with temperature has been theoretically investigated. W. M Cox and J. H. Wolfendon[8] were the first to draw attention towards the behaviour of B. They have suggested for the first time that just as the coefficient A accounts for the interionic forces, the coefficient B is presumably due to other effects characteristic of an ion and cation respectively.

Einstein[11] has given the following equation for the relative viscosity of a medium containing spherical porticles in suspension.

$$\eta = 1 + 2 \cdot 5v$$

where η is the relative viscosity of the suspensoid and v is the aggregate volume of the particles contained in 1 c.c. of the medium As the equation assumes that the spheres are large in comparison with the molecules of the suspending medium, a parallelism could be drawn between B and the linear term of the Einstein equation only in the case of ions of considerable size. With the assumption that they were restricted to ions whose temperature coefficient of mobility corresponds to the variation of fluidity of the solvent in the manner prescribed by Stokes law, they considered the coefficient B, like the linear term in the Einstein equation, as proportional to the ionic volume. They have calculated on this assumption the value of B at 18°C for the individual ions, in some cases.

We can associate the phenomenon of negative viscosity with the negative sign of the coefficient B. It was observed by Jones and Talley[1] that the coefficient B was negative for KCl and NH_4Cl at 18°C. Joy and Wolfendon[2] have got positive slope or positive value for B at 35°C for KCl and such a change in the sign of the slope may be expected in the case of NH_4Cl. In the present work both KCl and NH_4Cl show positive slope or positive value for B. So this tendency for the negative B coefficient to increase algebraically with rise of temperature can be explained by similar reasoning that is used in accounting for the change from negative to positive viscosity. Negative viscosity is mainly associated with the depolymerisation of the solvent molecules by the solute ions and hence a parallelism can be drawn between the diminished viscosity of water under high pressures and the electrostatic forces of ions in a solution.

At low temperatures water is considerably polymerised so that the ions can have their depolymerisation action to a marked extent. However at higher temperatures as water is already sufficiently depolymerised, there is not much scope for the action of the ions and their possible depolymerising effect is correspondingly reduced. This explains the change of sign of B with rise in temperature.

It is rather difficult to surmise anything about its nature merely from experimental observations. It was observed by

Sulston[4] that there was a tendency to increase in the value of B with temperature in the case of KCl and $MgSO_4$. It will be seen that there is definitely a tendency for B to increase with temperature in the case of KCl and NA_4Cl and an increase might be expected in the case of all others except LiCl. In the case of NaCl and $BaCl_2$ there is decrease again at 55°C. All the three salts—NaCl, $BaCl_2$, LiCl are highly hydrated and as the temperature rises there is thermal decomposition of hydrates and hydration decreases. Hydration contributes to increase in viscosity and this contribution tends to decrease with rise of temperature so we might expect a decrease in the value of the coefficient B which, as it is shown, appears to account for decrease in viscosity at high temperature particularly in the case of highly hydrated salts. Nothing more than this can be said about the nature of B unless more light is thrown on the whole phenomenon of electrolytic solutions.

SUMMARY

(1) The coefficients of viscosity of dilute aqueous solutions of the chlorides of lithium, sodium, barium, potassium, ammonium and calcium have been determined at three temperatures between 30° and 60°C for concentrations ranging from ·1 to ·01 mol. by means of a quartz viscometer wherein K. E. correction was quite negligible.

(2) An air thermostat was prepared working between the range 30° to 60° C.

(3) An account has been given of the different theories of viscosity of electrolytic solutions and results obtained are discussed in the light of the theories of electrolytes.

(4) The Jones and Dole equation is applied to the results obtained and the values of coefficients in the equation, as calculated from experimental data, are compared with those computed by Falkenhagen and Vernon on strict mathematical theory.

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CURVATURE OF SQUARE PLATES CLAMPED AT THE BOUNDARIES AND SUBJECTED TO A UNIFORM PRESSURE OVER ONE FACE

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The question of the elastic strength of flat plates freely supported or fixed at their edges and subjected to uniform loads upon their areas has been, from an engineering point, one of the many incompletely worked out and unsatisfactory parts of mechanics.

The analytical solution of the problem of the deformation of shells and plates under given forces and constrained under various boundary conditions has, for a long time, been a subject of great interest to mathematicians. Lame, Kelvin, De St. Venant and others have contributed much towards this particular branch and in recent years, several papers of great analytical interest have appeared in various scientific journals. All this information has been collected in various treatises on elasticity, Love's 'Treatise on Elasticity' being the chief one of them.

The problem, there, is a purely mathematical one, the object being to deduce differential equations for a plate from exact equations of elasticity. When an attempt is made to solve these equations for definite conditions such as with fixed or free boundaries, difficulties are encountered. Rigorous solutions have been obtained in the following cases only:—

(1) circular plates having free or fixed edges and being subjected to uniform or concentrated loadings;

(2) elliplical plates for free and fixed boundaries and subjected to uniform loadings; and

(3) plates having the shape of a lamican or cardioid.

Practical engineers have worked out empirical formulæ for the more useful cases of square and rectangular plates, but these formulæ have not been rigidly obtained.

The purpose of this work therefore was :—

(1) to solve the problem of square plates with the aid of *Retzs'* method[1] (which involves a series of successive approximations) ;

(2) to experimentally determine the displacement produced at various points over the surfaces of the square plates under uniform pressure ; and

(3) to see how far the theoretical calculations and the experimental determinations agree with each other.

THEORETICAL CALCULATIONS.

The equation to be satisfied by the normal displacement 'w' at any point on the plate when it is subjected to a pressure difference 'p,' is[2].

$$D\left(\frac{d^4}{dx^4}+\frac{2d^4}{dx^2\,dy^2}+\frac{d^4}{dy^4}\right)w=-p.$$

or more simply

$$D\nabla^2 w=-p \qquad \nabla \text{ standing for } \frac{d^2}{dx^2}+\frac{d^2}{dy^2}\Big]$$

where D is the flexural rigidity of the plate and is equal to

$$\frac{1}{12}\cdot\frac{Et^3}{1-\sigma^2};$$

'E' being the Young's Modulus, 'σ' the Poisson's ratio, and 't' the thickness of the plates.

The solution of this equation in case of square plates, fixed at the edges, must satisfy the conditions

$$w=0,\ \frac{dw}{dz}=0 \text{ and}$$

at the boundaries, $x=0$, $x=a$, $y=0$, $y=a$, where 'a' is the length of the plate, and the origin is at one corner of the square plate. The z axis is perpendicular to the plane of the plate. Gunjikar and Majumdar[3] have worked out an analytical solution of the above equation under the specified conditions by applying the method of Ritz[1] which is in the form of a series as follows:—

$$\frac{w}{l}=0\cdot674\ \xi_1\eta_1+0\cdot0308(\xi_1\eta_3+\xi_3\eta_1)+0\cdot0032\xi_3\eta_3$$
$$+0\cdot0040\ (\xi_1\eta_5+\xi_5\eta_1)+0\cdot0004(\xi_3\eta_5+\xi_5\eta_3)$$
$$+0\cdot0000\xi_5\eta_5$$

where[2]

$$\frac{10^4 l}{8a^4}=\frac{p}{\mathrm{D}}=\frac{12\,p\,(1-\sigma^2)}{\mathrm{E}t^3}$$

$$i.\ e.\quad l=\frac{96a^4(1-\sigma^2)}{\mathrm{E}t^3\times10^4}\,p$$

and where $\xi_n=\cos\frac{k_n x}{a}-\cosh\frac{k_n x}{a}-\left(\sin\frac{k_n x}{a}-\sinh\frac{k_n x}{x}\right)$

$$\frac{\cos k_n-\cosh k_n}{\sin k_n-\sinh k_n}$$

and η_n is a smilar function of y, and K_n is the nth root of the equation

$$\cos k_n \cosh k_n=1$$

x, y, being the coordinates of any point on the plate.

In order to calculate the theoretical values of the vertical displacements 'w' of the various points of the plates, the plate was divided into four equal quadrants by perpendicular bisectors of the side of the square plate. As the plate is symmetrical about the bisectors, the calculations of the displacement of any point in one of the quadrants will give naturally displacements of various points all over the plate.

The Apparatus: A circular block of steel, 'A' of diameter 32 cms. and thickness 3 cms. was machined as accurately as possible. A square recess of 1 cm. depth and 8 cms side was hollowed out at the centre of the block A. Sixteen thick bolts such as S were symmetrically fixed near the edge of the block about 14 cms. from the centre of A. A duct was drilled through the side of the block in order to put the central recess in connection with a compressed air cylinder.

Two identical steel discs B and C, of the same external dimensions as A were accurately machined. In the places corresponding to those of studs in the block A, sixteen holes were drilled in both B and C, so that the discs B and C could be made to coincide exactly with the block A. The studs were made long enough to be threaded to recieve nuts. These nuts, when well tightened clamped the two discs B and C to the block A. Symmetrically around the centres of the discs B and C, square apertures, of side equal to the side of the square plate under investigation, were cut out. The plate to be examined was placed between the discs B and C, and the discs were then screwed into the block A.

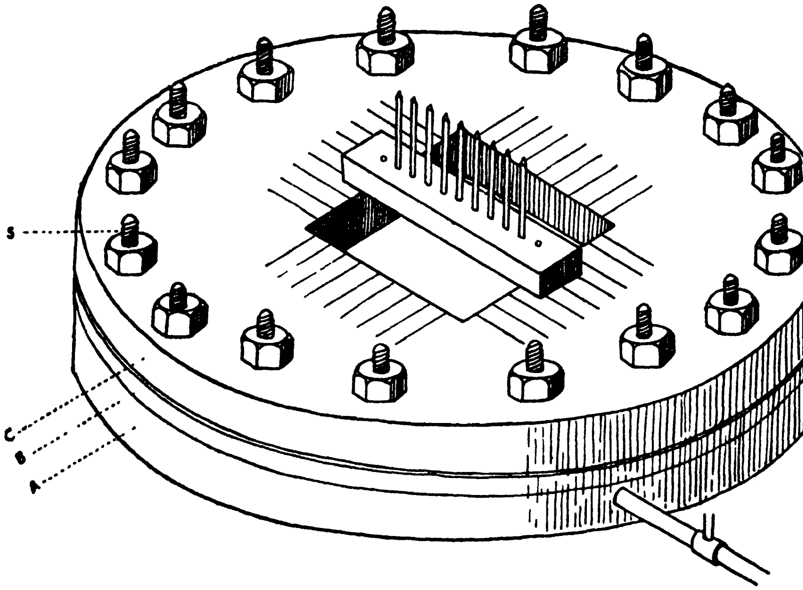

Fig. 1

The duct in the block A ended in a tube, which was brazed into an inverted T tube. The vertical end of the tube T was brazed into a pressure gauge, and the other end of the same was brazed into an inlet valve tube of a motorcar tube. The valve tube was connected to a compressed air cylinder. The air from the cylinder was then admitted into the recess till a required pressure was reached. It was found that, with proper washers between the plate and the discs, the pressure chamber can be filled with air at any desired pressure, and that the pressure can be maintained constant for a considerable length of time.

For the purpose of measurement, the edges of the square aperture on the upper disc C was divided (as shown in fig. 1) by a scale of centimetres, the zero of all the four scales being at the respective corners of the square. Use of a rectangular block of steel 16 cms. × 3 cms. × 1·5 cms. was made for marking the coordinates of the various points of the clamped plate. A series of holes, with their centres 1 cm. were drilled through this block. Vertical lines were etched on both edges of the block to mark the position of the axis along which the holes were drilled. By making these lines coincide with a particular division on either side of the aperture, the block could be placed to read the coordinates of any point on the unmarked clamped plate.

In order to read the displacements of various points (whose coordinates are now known), cylindrical rods, tapering to a point at both ends. were provided to fit the holes in the block. These rods, or pins, could slide up and down the holes smoothly without any lateral displacement. These pins were displaced vertically upwards when the clamped plate was subjected to a perssure from its lower face. The perpendicular displacements of the various points of the plate which is transferred to the pins, were read through a telescope mounted on a cathetometer.

The proper choice of plate was a difficult task. The plates had to be uniform at least in thickness. In order to ensure this brass plates were locally obtained and these were then rolled very carefully and by stages in a jeweller's rolling press until a desired thickness was obtained. From this plate, a square plate, was cut. The side of this plate was a little bigger than the required size. The reason for doing this was that whenever a plate is cut, a permanent strain is imparted near the boundaries of the plate. In order that this permanent strain near the edges may not affect the accuracy of experiments, slightly bigger sizes of plates were cut so that permanently strained region near the edges were outside the area where displacements were measured.

A number of plates of varying sizes and different thicknesses were measured under different pressures. Following is a typical set of results.

Side of the plate, a = 8 cms.
Thickness of the plate, t = 0·072 cms.
Pressure applied at one face = 9 lbs. per sq. inch,

$\frac{y}{a}$	Values (in cm.) of the Deflection										
0·5000	Calculated	...	0·0054	0·0185	0·0375	0·0498	0·0635	0·0741	0·0807	0·0831	
	Observed	...	0·0100	0·0228	0·0376	0·0483	0·0611	0·0725	0·0792	0·0802	
0·3750	Calculated	...	0·0049	0·0163	0·0305	0·0446	0·0571	0·0661	0·0720	0·0741	
	Observed	...	0·0080	0·0193	0·0295	0·0421	0·0554	0·0642	0·0711	0·0725	
0·2500	Calculated	...	3·0033	0·0113	0·0209	0·0306	0·0383	0·0446	0·0485	0·0498	
	Observed	...	0·0056	3·0130	0·0205	0·0291	0·0363	0·0421	0·0466	0·0483	
0·1250	Calculated	...	0·0013	0·0041	0·0077	0·0113	0·0140	0·0163	0·0177	0·0185	
	Observed	...	0·0002	0·0051	0·0093	0·0130	0·0165	0·0193	0·0220	0·0228	
			0·0625	0·1250	0·1875	0·2500	0·3125	0·3750	0·4375	0·5000	$\frac{x}{a}$

From a number of such tables indicating values of calculated and observed deflections for plates of various sizes and thicknesses

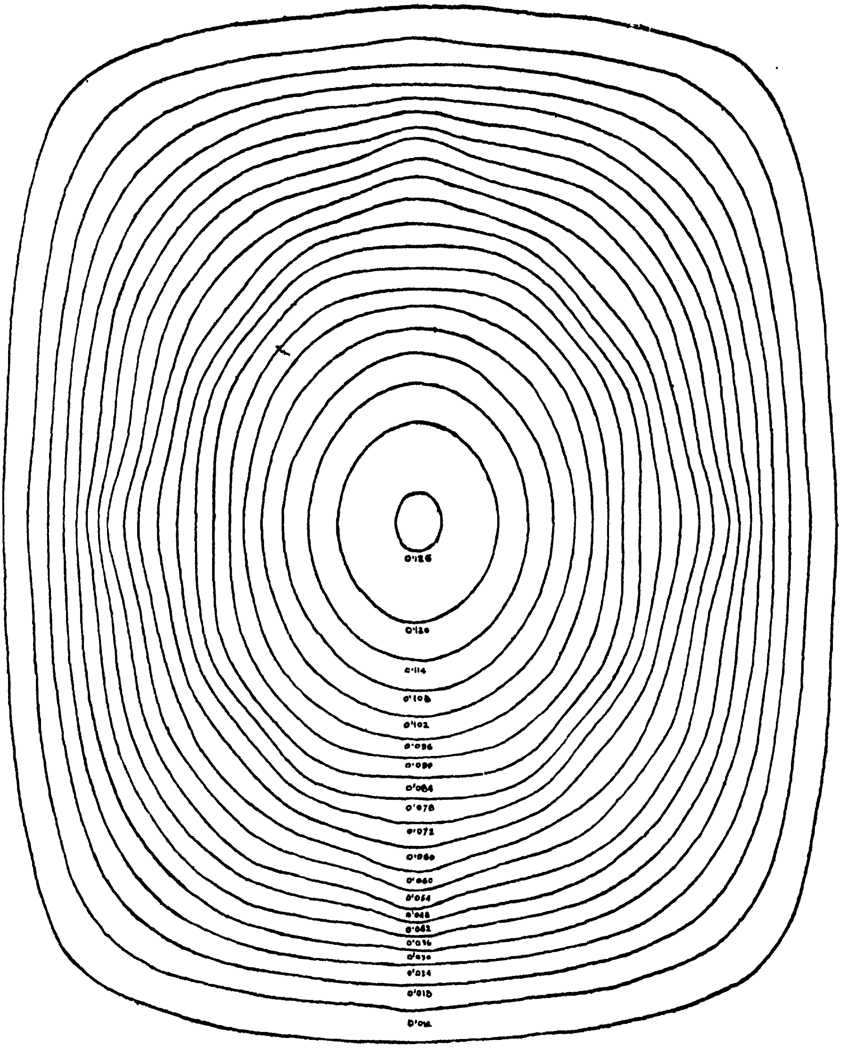

Fig. 2

and subjected to different pressures, very consistent conclusions were arrived at. In order to compare the calculated and observed values of the deflection, graphs of deflections of various points lying on a straight line parallel to one of the edges against their distances from one end of the straight line were ploted. A contour map for a given deflection at various points of the plate of given size and subjected to a known pressure was also drawn. Till now, it has been a matter of argument whether in a square plate clamped at the boundaries and subjected to a uniform pressure over one face, maximum strain was along the diagonals of the square or along the diameters. The series of graphs and contour maps conclusively demonstrated the important fact that the maximum strain is along the diameters (Fig. 2.).

Conclusions

(1) The calculated values of the deflections at various points agree well with those measured by experiments, except for those points that are situated near the edges. These deviations from the theoretically calculated values can be accounted for by taking into consideration the fact that the edges could not exactly be clamped at the boundaries of the apparatus but were actually clamped at little distances outside the actual boundary of the edges. In other words the side of the plate was clamped a little beyond the boundaries of the aperture, *i.e.* the side of the plate was a little larger than the size actually measured. In that case observed deflection is bound to be larger than the calculated one. This fact is borne out by comparing the two values of the deflection near the edges.

(2) The shape assumed by a plate is not materially affected by small alteration in pressure, but is materially altered by a small alteration in size of the plate.

(3) The maximum strain lies along the diameters of the plate and not along the diagonals.

Our thanks are due to Professor G. R. Paranjpe who has given us valuable advise from time to time throughout the period during which these experiments were carried out.

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STUDY OF THE RELATIVE INFRA-RED CONTENT OF SOLAR RADIATIONS AT BOMBAY

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In the study of solar radiations undertaken in this laboratory, we have already reported in two papers,[1, 2] the methods of investigation and estimation of ultra-violet content of sunlight at Bombay. In the present paper, we have confined our attention to infra-red portion, the preliminary investigations in which have yielded some consistent results which, it is thought, would be of some value in sun-ray therapy.

The solar radiations in the infra-red region, before they reach the earth, are subject to considerable absorption in the intervening atmosphere. This is due chiefly to water vapour and carbon-dioxide, which have marked absorption bands in the near infra-red. It is only on account of the sun's intensity which is much greater than any of the terrestrial sources, that we are able to detect an appreciable infra-red radiation even after the absorbing layer of the atmosphere.

The problem of isolating, indentifying and detecting a particular band of wave-length region in the infra-red is beset with many experimental difficulties. Consequently data in this part of the spectrum is not as prolific as we have it for other regions. The entire infra-red scale of electromagnetic radiations is much more extensive than the whole of ultra-violet and visible portions. Leaving the ultra-violet and the visible which are amenable to photographic methods out of our consideration, we have from 0. 7μ onwards, a band which can well be separated into two portions—one extending upto about 25μ, called the near infra-red and the other beyond 25μ, called the far infra-red. The methods of isolating and detecting differ according to the type of work under investigation. The object of the present investigation is to determine the ratio of infra-red energy to the effective total energy of the sun. The lowest limit of wave-length for the transmission of solar energy is 2900 A°, as indicated by Ramnathan and Ramdas [3] and by Tawde, Trivedi and Patel [1]. We have no such knowledge of the highest limit in the infra-red.

EXPERIMENTAL.

A beam of sunlight was allowed to fall on a plane mirror of stainless steel of large aperture. By a second reflection from a similar but concave mirror, it was allowed to fall on a thermopile over which the amount of radiation was regulated by a slit. It was not found necessary to employ a very sensitive thermopile as smallest slit-width gave a very large deflection with ordinary thermopile. The latter was connected to a very sensitive Pye galvanometer of ballistic type. The deflections were sufficiently magnified by placing the scale at a distance of about two meters from the oscillating mirror system. The apparatus was kept in a room which was liable to be least affected by external temperature fluctuations. The thermopile was isolated and kept at a great distance from the observer in order to minimize the temperature changes. With all these precautions observations were taken only after the room and the whole apparatus were allowed to attain the temperature equilibrium. Care was taken to see that the opening through which the reflected beam of sunlight was admitted into the room did not disturb this equilibrium. No dispersing system was employed to obtain a particular spectral band but requisite filters were used to transmit a composite beam of radiations lying within particular wave-length limits. It may be noted that experimental technique of similar nature has been employed by Vafiadi, Krivich, and Pokrovsky[4] in investigations of solar radiations in the extreme infra-red beyond 400μ.

The procedure followed in taking the observations was to note down the steady deflection of galvanometer when the beam was allowed to fall on the thermopile without any filter. This deflection was taken to be proportional to the effective solar energy. The beam was then completely cut off from the thermopile and the galvanometer allowed to attain zero corresponding to normal dark conditions. It was found that the galvanometer showed good recovery towards the original zero. A Kodak infra-red filter stopping rays below $0{\cdot}6\mu$ was then interposed in front of the slit of the thermopile and the deflection again noted when the beam was allowed to pass through it. The infra-red filter cut off all visible and ultra-violet radiations allowing only the near and far infra-red to pass. The deflection obtained under these conditions was thus proportional to the total infra-red energy. By using fluorspar plate as filter, the far infra-red only beyond 25μ can be cut off from the solar energy. The infra-red filter together with fluorspar plate give deflections which can be said to be proportional to the the near infra-red. If d_1 is the direct reading without any filter

TABLE I

Values of σ (Date 24–11–37)

Kodak filter.		Agfa filter		Kodak filter. fluorspar plate		Agfa filter. fluorspar plate.		Fluorspar plate.	
Time.	σ	Time.	σ	Time.	σ	Time.	σ	Time.	σ
11–36 A.M.	32·33	11–42 A.M.	30·37	12–0 Noon	21·61	11–54 A.M.	24·15	11–49 A.M.	85·89
12–57 P.M.	30·00	1–7 A.M.	30·86	1–30 P.M.	25·41	1–21 P.M.	26·57	1–14 P.M.	83·67
2–0 P.M.	29·13	2–6 P.M.	29·48	2–36 P.M.	31·01	2–17 P.M.	25·37	2–13 P.M.	(77·69)?
3–7 P.M.	32·43	2–48 P.M.	32·69	2–45 P.M.	26·38	2–42 P.M.	24·48	2–38 P.M.	89·43
3–33 P.M.	26·33	3–39 P.M.	25·67	4–1 P.M.	25·61	3–53 P.M.	20·75	3–47 P.M.	86·68
Mean	30·044	Mean	29·81	Mean	26·004	Mean	24·26	Mean	84·67

TABLE II

Values of σ (Date 25–11–37)

11–27 A.M.	30·91	11–31 A.M.	28·74	11–55 A.M.	21· 1	11–40 A.M.	23·42	11–35 A.M.	77·24
11–55 A.M.	32·61	12–0 Noon	31·78	12–11 P.M.	23·24	12–6 P.M.	23·75	12–2 P.M.	79·26
12–28 P.M.	31·20	12–33 P.M.	30·65	12–39 „	28·07	12–42 „	27·63	12–35 „	81·07
12–57 „	28·44	12–55 „	26·95	1–7 „	21·85	1–3 „	24·01	1–0 „	76·44
1–20 „	31·30	1–29 „	32·00	1–47 „	25·71	1–45 „	22·79	1–40 „	87·60
2–13 „	29·91	2–30 „	29·27	2–20 „	26·20	2–25 „	24·06	2–18 „	75·23
2–54 „	27·36	3–0 „	29·31	3–20 „	(16·85)	3–15 „	21·15	3–12 „	89·76
3–37 „	33·07	3–45 „	31·62	4–1 „	21·76	3–58 „	22·79	3–52 „	90·30
Mean	30·60	Mean	30·04	Mean	23·19	Mean	23·70	Mean	82·11

TABLE III

Values of σ (Date 23–11–37)

1–18 P.M.	27·94	1–25 P.M.	29·83	1–43 P.M.	20·01	1–41 P.M.	19·85	1–30 A.M.	80·59
1–52 „	29·64	1–54 „	29·69	2–18 „	24·48	2–14 „	22·38	2–8 „	80·99
Mean	28·79	Mean	29·76	Mean	22·24	Mean	21·11	Mean	80·79

and d_2 through any filter, then the percentage ratio of filtered radiations to the total effective energy is expressed as

$$\sigma = \frac{d_2}{d_1} \times 100.$$

This value of σ has no absolute significance unless we take into account absorption co-efficient of the filter for the particular rays it can transmit. However, this does not prevent us from studying the relative variation of σ under uniform conditions with different hours of the day, which we have done in the present paper. Appreciable time elapses between the readings d_1 and d_2. A correction is therefore applied to d_1 by drawing a graph of time against deflections d_1 and reading from it the value of d_1 at the instant when d_2 was observed. The nature of these graphs can be studied from fig. 1 where data for two days are recorded. In Tables I, II, III, we have given a record of observations of σ made on three days (*viz.* 23rd, 24th, & 25th Nov. 1937). In figs. 2 & 3, these readings are interpreted graphically.

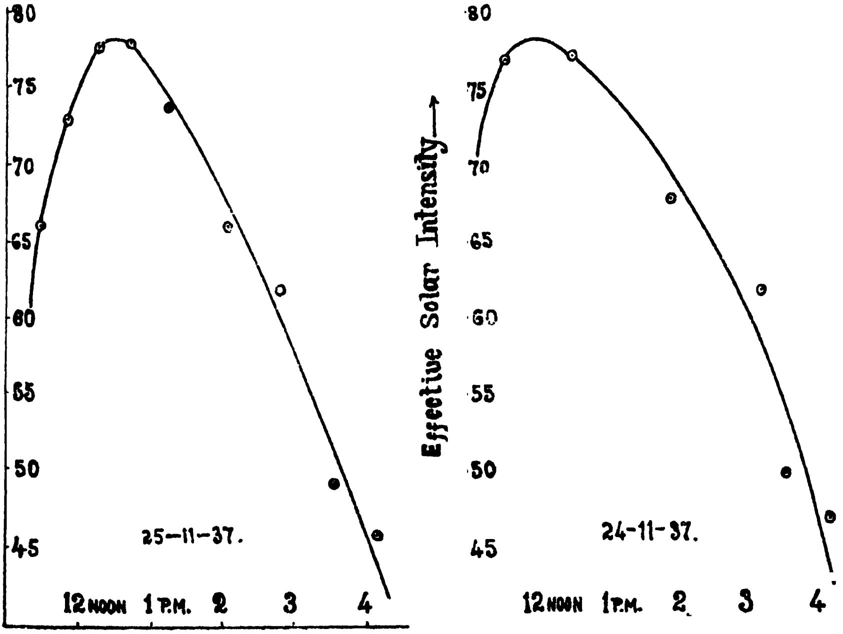

FIG. 1

CONCLUSIONS

It may be seen from the graphs that the values of σ do not vary systematically over the observed period on any of the two days. This shows that the relative infra-red content remains practically constant for the greater part of solar intensity. A mean value of readings in each case has been shown by a thick horizontal line in the graphs which enables us to conclude that infra-red

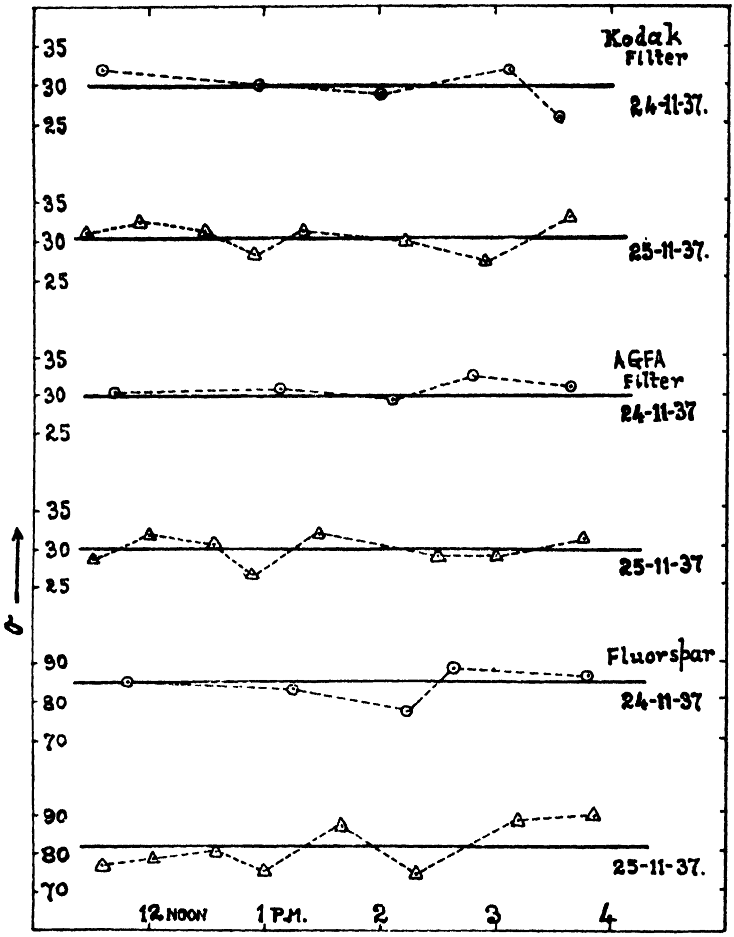

FIG. 2.

energy bears, during day time, a constant ratio with the effective total intensity of the sun. The fluctuations from the mean are likely to result from wind velocity, humidity etc. As a rough estimate, which is likely to involve an error of about 12 to 15%, we are giving below the relative percentages of available solar energy in the different regions. For estimating the proportion of visible to ultra-violet, we have utilized the results of Tawde, Trivedi & Patel[1] which are much more accurate.

Far Infra-red : 6%
Near Infra-red : 24%
Visible region : 56.7%
Ultraviolet : 1.3%

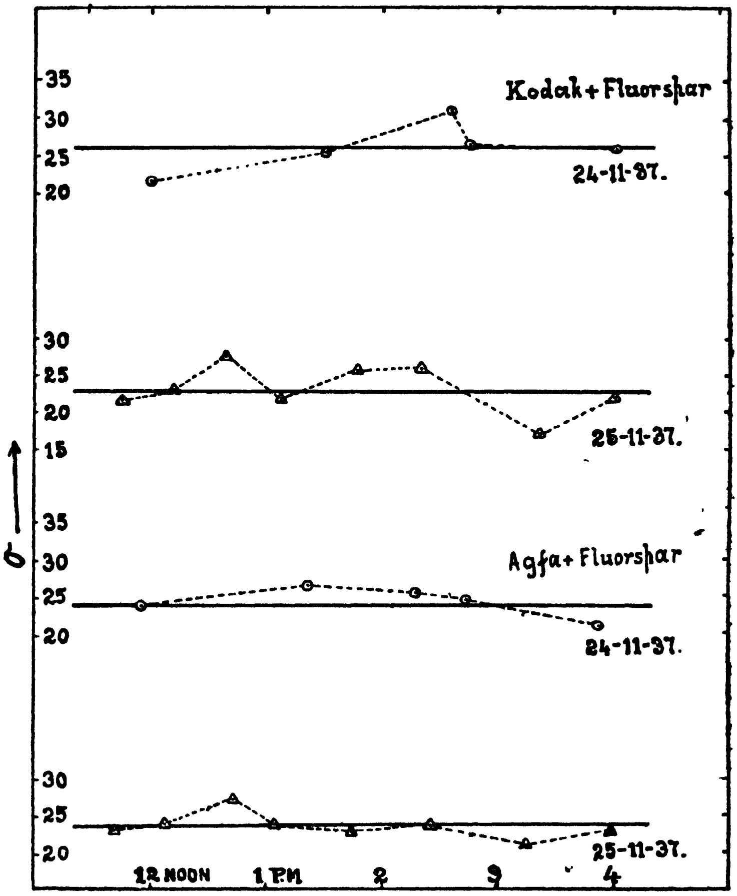

FIG. 8.

It would be of interest to extend these observations further at different heights from sea-level and from before the sunrise till after the sunset.

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DIAMAGNETISM AND COLLOIDAL ELECTROLYTES

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Colloidal electrolytes have created a keen and everincreasing interest during the last twenty years. Duclaux[1] introduced the notion of a colloidal electrolyte for the first time. Colloidal electrolytes are those which exhibit the properties characteristic to colloids in regard to dialysis and Tyndall phenomenon, but at the same time behave as good electrolytes. They manifest the characteristic property of electrical conductivity. They can easily be divided into the following three groups :—

1. The colloidal electrolytes which are sensible to dilution but form ions which can be dialysed. Soaps when dissolved in a suitable solvent such as water, show the above mentioned behaviour.

2. The colloidal electrolytes which are sensible to dilution but form ions which cannot be dialysed. Cetyl sulphonic acid and its salts, long chain amino compounds and many dye-stuffs of the Congo group exhibit this second type of colloidal phenomenon.

3. The colloidal electrolytes that are practically not sensible to dilution. Many proteins have large molecular weights and are good electrolytes. They belong to the third type of colloidal electrolytes. The prominent investigators, who have rendered valuable contributions in this domain are McBain[2], Meyer, Schaffer and Terroine[3], Hardy[4], McBain, Laing and Titley[5], Taylor[6], Bowden[7], Fischer and Hooker[8], Duclaux[1], Malfitano[9], Leimtorfer[10], Biltz[11], Garner[12], Zeigmondy[13], Lottermoser[14], Freundlich and Farmer[15], Harman[16], Spychalski[17], Hartley[18], Rysselberghe[19], Robinson and Moilliet[20], Gehart and Weitendorf[21].

The present investigations are confined to the electrolytes of the first type only. McBain and his collaborators have made a special study of soaps. They have investigated the physical properties such as conductivity and hydrolysis of the alkali salts of fatty acids ascending in a homologous series. The lower members are strong electrolytes but the higher ones show distinct anomalies. This anomalous behaviour has been attributed to micelles consisting of large particles of colloidal dimensions built of a large number of monomeric anions of the fatty acids, containing alkali metal as well.

Magnetic study of many elements and compounds in the colloidal state has been made by several investigators. Nobody, however, seems to have dealt with the problem of colloidal electrolytes magnetically, except Bhatnagar and Kapur. They have found the magnetic rotations for some salts of higher fatty acids and have produced evidence of the formation of ionic micelle. The present investigation has been undertaken in order to study their diamagnetism in the solid phase and to throw further light on their constitution.

EXPERIMENTAL

The method described by McBain was followed in preparing the colloidal electrolytes. Alcoholic solutions of potassium and sodium hydroxide were mixed gradually with the alcoholic solutions of fatty acids. Phenolphthalein was used as an indicator. The salts were dried in a vacuum desiccator till they were completely free from alcohol. The susceptibilities of the colloidal electrolytes were determined by a suitably modified form of Gouy's balance. The calculations were made according to the equation :

$$xd_2 = \frac{1}{md_2}\left[(xd_1 md_1 - x_a m_a d_1)\ \frac{wd_2}{wd_1} + x_a m_a d_2 \right]$$

where xd_1 = specific susceptibility of the standard substance.

xd_2 = specific susceptibility of the specimen.

wd_1 = pull due to the standard substance.

wd_2 = pull due to the specimen.

md_1 = mass of the standard substance.

md_2 = mass of the standard specimen.

$m_a d_1$ = mass of air displaced by the standard substance.

$m_a d_2$ = mass of air displaced by the specimen.

EXPERIMENTAL RESULTS

TABLE I

Specific and Molecular Susceptibilities of Some Fatty Acids

Substance	Specific Susceptibility $-\chi \cdot 10^6$		Molecular Susceptibility $-\chi^M \cdot 10^6$		
	Observed	Other authors	Observed	Other authors	Calculated according to Pascal
Acetic Acid CH_3COOH	0·532	0·526 Pascal 0·535 Cabrera and Fahlenbrach 0·534 Kido	31·9	31·6 Pascal 32·0 Kido 32·1 Cabrera and Fahlenbrach	31·85
Propionic Acid C_2H_5COOH	0·592	0·587 Pascal 0·586 Kido	43·8	43·6 Pascal 43·5 Kido	43·75
Butyric Acid C_3H_7COOH	0·635	0·632 Pascal	55·9	55·7 Kido 55·6 Pascal	55·65
Palmitic Acid $CH_3(CH_2)_{14}COOH$	0·775		198·6		198·45
Stearic Acid $CH_3(CH_2)_{16}COOH$	0·776		220·8		222·25
Oleic Acid $CH_3(CH_2)_7C.H$ $H.C(CH_2)_7COOH$	0·739	0·742 Pascal	208·5		210·65
Myristic Acid $C_{13}H_{27}COOH$	0·770		176·0		174·65

TABLE II

Specific and Molecular Susceptibilities of Some Potassium and Sodium Salts of Lower Fatty Acids

Substance	Specific Susceptibility $-\chi\cdot10^6$		Molecular Susceptibility $-\chi_M\cdot10^6$		
	Observed	Other authors	Observed	Other authors	Calculated according to Pascal
Sodium acetate $CH_3\cdot COONa$	0·45	0·483 Kido from hydrate	36·9	39·6 Kido	38·1
Sodium propionate C_2H_5 COONa	0·503		48·3		50·0
Sodium butyrate C_3H_7 COONa	0·552		60·7		61·9
Potassium acetate CH_3 COOK	0·463	0·458 Kido 50% soln	45·4	45·0	47·4
Potassium propionate C_2H_5 COOK	0·505		56·6		59·3
Potassium butyrate C_3H_7 COOK	0·553		69·7		71·2

TABLE III.

Specific and Molecular Susceptibilities of Higher Fatty Acids. Salts of Potassium and Sodium.

Substance.	Specific susceptibility observed.	Molecular Susceptibility $-\chi\cdot10^6$	
	$-\chi\cdot10^6$	Observed.	Calculated according to Pascal.
Sodium palmitate $CH_3(CH_2)_{14}COONa$	0·712	198·6	204·7
Sodium stearate $CH_3(CH_2)_{16}$ $COONa$	0·722	221·1	228·5
Sodium oleate $C_{17}H_{33}COONa$	0·685	208·4	216·7
Sodium myristate $C_{13}H_{27}COONa$	0·707	176·8	180·9
Potassium palmitate $CH_3(CH_2)_{14}COOK$	0·701	206·3	214·0
Potassium stearate $CH_3(CH_2)_{16}COOK$	0·712	229·6	237·8
Potassium oleate $CH_3(CH_2)_7\cdot CH$ $CH(CH_2)_7COOK$	0·673	215·6	226·2
Potassium myristate $C_{13}H_{27}COOK$	0·692	184·3	190·2

DISCUSSION OF RESULTS.

Sodium and potassium salts of fatty acids were prepared from the corresponding fatty acids. In order to be sure about the purity of the fatty acids employed, their specific and molecular susceptibilities were determined and compared with other experimental and theoretical values. From the results given in Table I it is evident that there is a close agreement between them.

Similar agreement between the theoretical and experimental diamagnetic susceptibilities of potassium and sodium salts of lower fatty acids has been obtained within the experimental error (see Table II). On the other hand, the diamagnetic susceptibilities of sodium and potassium salts of higher fatty acids do not obey the general additive law. The experimental diamagnetic susceptibilities of these salts are decidedly lower than the theoretical ones. It is evident from this that the constitutions of the salts of higher fatty acids are quite different from those of the lower fatty acids. McBain and his collaborators have shown that the lower members of the alkali salts of fatty acids are strong electrolytes while the higher ones show distinct anomalies, This anomalous behaviour has been attributed to the micelle consisting of large particles of colloidal dimensions built of a large number of monomeric anions of the fatty acids containing alkali metal as well. In order to bring this point into prominence, activity coefficients or degree of dissociation along with those of KCl solutions have been given in the following table,

TABLE IV.

Activity Coefficients of some Solutions.

Molality.	K-acetate.	K-Palmitate	K-Myristate.	Na-acetate	Na-Palmitate.	Na-Myristate	KCl
0·01	0·8	0·88	0·89	0·87	0·89	0·89	0·903
0·02	0·7	0·83	0·84	0·79	0·85	0·85	0·874
0·05	0·53	0·70	0·74	0·63	0·75	0·76	0·822
0·10	0·39	0·57	0·61	0·48	0·69	0·66	0·772
0·20	0·26	0·40	0·46	0·33	0·48	0·52	0·715
0·30	0·20	0·31	0·37	0·26	0·37	0·42	0·693
0·40	0·16	0·25	0·31	0·21	0·30	0·34	0·667
0·50	0·13	0·21	0·26	0·17	0·24	0·29	0·651
0·80	0·08	0·14	0·17	0·11	0·16	0·20	0·617
1·00	0·07	0·11	0·14	0·09	0·13	0·16	0·601

It is evident from this table that the activity coefficients or the degrees of dissociation of higher concentrations of soap solutions are very much smaller in comparison with those of strongly electrovalent salt, namely potassium chloride. Covalent salts are generally distinguished from the electrovalent ones by their smallness in sizes and degrees of dissociations. Thus, the smaller the degree of dissociation, the smaller is the size of the salt concerned. From the general expression of the ionic susceptiblity:

$$\chi_{\text{ion}} = \frac{Ne^2}{6Mc^2}\sum_n r^{-2} = 2\cdot832\cdot10^{10}\sum_n r^{-2}$$

it is obvious that the diamagnetism of an ion depends on the numerical value of $\sum_n r^{-2}$. If the value of $\sum_n r^{-2}$ changes the ionic value χ_{ion} also changes accordingly. The alkali salts of higher fatty acids being weak electrolytes, should, therefore, have lower diamagnetic values than the theoretical ones. The present lower diamagnetic susceptibilities obtained for them are therefore in line with this view. Further similar explanations have been put forth by Hocart[22] and Brindley and Hoare[23]. The susceptibility of a heteropolar salt, both as a solid and in solution is considered to be the sum of the susceptibilities of positive and negative ions.

$$\chi_M = \chi_{\text{ion}^+} + \chi_{\text{ion}^-}$$

Many a time, the states of ions are different under different conditions. If the symbols F, C and D are introduced to signify the ions as free, solid (in crystals) and dissolved, it would be expected that χ_C and χ_D would be less then χ_F owing to the limitation of the effective spread of the electron density distribution and thereby deforming the radii of the ions on which the diamagnetism depends. Generally, it has been found that the diamagnetic susceptibility of salts in solution is slightly higher than that in the sold state. Thus the formation of micelles of a large number of monomeric anions of the fatty acids containing alkali metals, the abnormal behaviour towards electrolytic dissociation, the deformation in an ionic radii owing to the limitation of the effective spread of the electron density distribution and the lower diamagnetic suceptibilities of the alkali salts of higher fatty acids clearly establish the fact that the constitutions of the higher members of the alkali salts of fatty acids are quite different from those of the lower members of the same series.

My thanks are due to Professor S. S. Bhatnagar for his help during the course of the present investigation.

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DIAEAGNETISM OF SOME INORGANIC LIQUID COMPOUNDS.

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The constitution of many organic liquids has been critically examined magnetically by several workers. Further, the influence of temperature on them has also been the subject of investigation for a long time. The large number of organic compounds existing in the liquid form and the ease with which they are found in a higher state of purity and stability, are mainly responsible for it. However, the commonest liquid, i. e. water, and some other mineral acids such as hydrochloric acid, sulphuric acid and nitric acid are the substances which have been studied much more extensively. Further, some liquid halides of silicon, antimony, tin, phosphorus and sulphur have been investigated by Pascal[1], Farquharson[2], Kido[3] and Varadachari and Subramaniam[4]. The inferences derived by them regarding their constitutions are not consistent. It was, therefore, felt desirable to investigate them in order to throw further light on their constitutions, paying due regard to the purity of the substances employed.

EXPERIMENTAL.

The apparatus employed for the determination of magnetic susceptibilities of inorganic liquids was the modified form of Gouy's balance. According to this method the susceptibilities can be calculated by the equation;

$$xd_2 = \frac{1}{md_2}\left[(xd_1 \, md_1 - x_a m_a d_1) \frac{wd_2}{wd_1} + x_a m_a d_2 \right]$$

where xd_2 = the magnetic susceptibility of the specimen.
xd_1 = the magnetic susceptibility of the standard substance.
md_2 = mass of the specimen.
md_1 = mass of the standard substance.
x_a = magnetic susceptibility of air.
$m_a d_1$ = mass of the air which fills the same volume as the substance d_1.
wd_2 = pull due to the substance d_2.
wd_1 = pull due to the substance d_1.
$m_a d_2$ = mass of the air which fills the same volume as the substance d_2.

Some of the substances employed were prepared in the laboratory. Their physical properties such as boiling points and densities were measured and compared with those given in the standard literature. Only those substances, which proved to be quite pure, were taken for the magnetic measurements.

EXPERIMENTAL RESULTS

TABLE I.

Specific Diamagnetic Susceptibilities of some Inorganic Liquid Compounds.

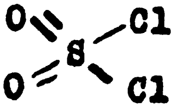
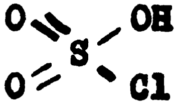
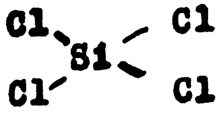
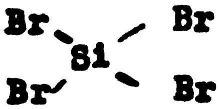
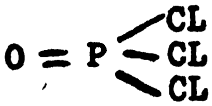
Substance	Structural formula	Specific Susceptibility $-\chi\cdot10^6$	
		Observed	Other authors
SCl_2	Ct—S—Cl	0·478	0·478 Kido 0·467 Varadachari and Subramaniam.
S_2Cl_2	$S=S=Cl_2$	0·405	0·461 ,,
$SOCl_2$	$O=S=Cl_2$	0·380	0·451 Kido 0·372 Varadachari and Subramaniam.
SO_2Cl_2		0·397	0·402 Kido 0·365 Varadachari and Subramaniam.
SO_3HCl		0·402	0·400 Kido
$SiCl_4$		0·497	0·518 Kido
$SiBr_4$		0·362	0·360 Pascal
ICl	T−Cl	0·350	0·336 Kido
$POCl_3$		0·403	0·449 Kido

TABLE II.

Molecular Susceptibilities of some Inorganic Liquid Compounds

Substance	Molecular Susceptibility $\chi_M \cdot 10^6$	
	Observed	Other authors
SCl_2	49·2	49·4 Kido 48·1 Varadachari and Subramaniam
S_2Cl_2	54·7	62·2 „ „ „
$SoCl_2$	45·2	53·2 Kido 44·3 Varadachari and Subramaniam
SO_2Cl_2	53·6	54·6 Kido 49·3 Varadachari and Subramaniam
SO_3HCl	43·9	46·6 Kido
$SiBr_4$	126·0	...
$SiCl_4$	84·6	87·4 Kido
$POCl_3$	61·8	68·9 Kido
ICl	56·8	54·6 Kido

DISCUSSION OF RESULTS

It is legitimate to regard the molecular susceptibility as the sum of constitutive ionic susceptibilities for definitely hetero-polar salts. In the inorganic liquid compounds that have been examined presently, the typical linkage is more or less covalent. It is, therefore, evident that the above law is not valid in finding out the susceptibility constants from them. The susceptibilities of organic covalent compounds have been found out by Pascal by the expression :

$$\chi_M = \Sigma_{nA}\, \chi_A + \lambda$$

where n_A is the number of atoms of susceptibility χ_A and λ is the constitutive factor depending on the nature of the linkages between the various atoms. This expression can very well be applied in the present inorganic liquid compounds. Kido[5], Gray and Cruickshank[6] have recently made some modifications in the above Pascal's additive law to some extent. However, the values obtained by Gray and Cruickshank are not different from those that are obtained by Pascal. With all its limitations the additivity law of Pascal and his constitutive corrections are, therefore, the best for the present in dealing with covalent compounds. Pascal's values for various atoms have, therefore, been used in the present investigation. Further, it will be seen that better results are obtained by following Pascal while finding out the susceptibility constants of different elements in various valency states.

SCl_2:—

The structural formula of SCl_2 is Cl–S–Cl. The specific and molecular susceptibilities of SCl_2 closely correspond with those obtained by Kido, Varadachari and Subramaniam within the experimental error. While finding out the susceptibility constant for sulphur in the divalent state Pascal's value, 20.1, for chlorine has been used. The constant comes out to be $-9\cdot10^{-6}$. In the following table the different values obtained by various authors are given.

TABLE III.

Susceptibility Constants for Divalent Sulphur.

$-\chi\cdot10^{6}$

Theoretical.		Experimental.	
Slater	12·13	Kido	5·2
Angus	11· 0	Gray and Farquharson	14·7
		Observed.	9·0

The present experimental value 9 is nearer to 11 obtained by Angus. The lower value 5·2 obtained by Kido is due to the higher values of chlorine taken by him. If he had substituted Pascal value 20·1 for chlorine, he would have got the same constant 9·2 instead of 5·2.

S_2Cl_2 and SO_2Cl_2:—

The structural formula for S_2Cl_2 are Cl–S–S–Cl and S = S = Cl_2. The latter has been proved to be correct due to its similarity in its properties with O = S = Cl_2 and confirmed also on spectroscopical evidence. The specific susceptibility of $SoCl_2$ is $-0\cdot380\cdot10^{-6}$ and closely correponds with $-0\cdot372\cdot10^{-6}$ obtained by Varadachari and Subramaniam. Kido's value $-0\cdot451\cdot10^{-6}$ is rather high. Similarly the specific susceptibility $-0\cdot405\cdot10^{-6}$ for S_2Cl_2 is quite different from $-0\cdot461\cdot10^{-6}$ derived by Varadachari

Subramaniam. However, it will be seen that the present values fit in well, while finding out the constants for sulphur in the tetravalent state. Substituting Pascal's values for chlorine and oxygen and the value 9 that is obtained for the divalent sulphur, the susceptibility constants for tetravalent sulphur come out to be 5·5 and 6·8 from S_2Cl_2 and $SOCl_2$ respectively. The values 5·5 and 6·8 are decidedly different from the values 9 obtained for divalent sulphur. In the following table the experimental as well as theoretical constants are given.

TABLE IV

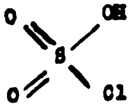
Susceptibility Constants for Tetravalent Sulphur.

$-\chi \cdot 10^6$			
Theoretical.		Experimental	
Slater	5·73	Kido	−4·6
Angus	5·6	Gray and Farquharson	7·4
		Observed	5·5 6·8

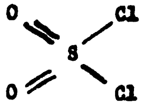
The observed values 5·5 and 6·8 are in agreement with the theoretical values 5·73 and 5·6 derived by Slater and Angus on the one hand and the experimental one 7·4 obtained by Gray and Farquharson on the other. Kido's value −4·6 for tetravalent sulphur is unexpectedly low and paramagnetic. It is perhaps due to the different values he takes for chlorine for substitution. Further, no definite conclusions can be drawn from the results of Varadachari and Subramaniam as they have not discussed the subject in the light of similarity in structure beween S_2Cl_2 $SOCl_2$.

SO_2Cl_2 and SO_3HCl :—

It has been proved from an examination of different physical properties that SO_2Cl_2 and SO_3HCl have the structural formulae



and



The specific and molecular susceptibilities obtained by the author and by Kido for SO_2Cl_2 and SO_3HCl are almost the same, but the values of SO_2Cl_2 obtained by Varadachari and Subramaniam are rather low. By substitution of OH group by chlorine in SO_3HCl the compound SO_2Cl_2 is obtained. Naturally, the difference between their molecular susceptibilities should be the difference in the susceptibilities of chlorine and OH group. According to Pascal it should be 12·5. As a matter of fact it comes out to be rather low. Kido also has not explained this anomalous behaviour. However, the difference obtained by the author and by Kido is almost of the same order.

$SiBr_4$ and $SiCl_4$:—

The specific and molecular susceptibilities closely correspond with those obtained by Kido and Pascal. Substituting Pascal's values for chlorine and bromine the susceptibility constants for tetravalent silicon come out to be 3·6 and 4·2. The different experimental and theoretical susceptibility constants for tetravalent silicon are given in the following table.

TABLE V

Susceptibility Constants for Tetravalent Silicon

		$-\chi\cdot10^6$			
Theoretical				Experimental	
Pauling	2·1	...	...	Kido	−1·0
Slater	2·03	...	...	Observed	4·2
Angus	1·87	...	...		3·6

If Kido had substituted Pascal's value for chlorine, 20·1, he would have also obtained almost the same value as has been observed by the author. Further, the present results are not far away from the theoretical ones obtained by Pauling, Slater and Angus.

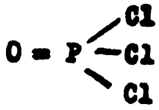
ICl :—

The specific and molecular susceptibilities are very near to those obtained by Kido. Gray and Farquharson however, get quite different values for them. Naturally, the susceptibility constant 36·7 for monovalent iodine is in agreement with 34·3 obtained by Kido, while Gray and Farquharson have found it to be 57·27. On the other hand, the theoretical suceptibility constants for monovalent iodine are 40·3 and 40·5 according to Slater and Angus, respectively. The values obtained by the author and by

Kido are nearer to those determined by Slater and Angus than that of Gray and Farquharson.

$POCL_3$:—

The structural formula of $POCL_3$ is



Subtracting the proper values of chlorine and oxygen, the susceptibility constant for pentavalent phosphorus comes out to be 3·3, while Kido gets a value of −8·0. Theoretical values for pentavalent phosphorus are 1·7, 1·66 and 1·54 obtained by Pauling, Slater and Angus, respectively. The present value 3·24 fulfils the theoretical expectation better than that of Kido.

From the survey of the above discussion of results it is rather interesting to note that by following Pascal, better susceptibility constants are obtained for sulphur in various valency states, monovalent iodine, tetravalent silicon and pentavalent phosphorus.

The present writer expresses his indebtedness to Prof. S. S. Bhatnagar for his kind advice and help during this work.

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SIMPLE ANALYTICAL DERIVATIONS OF THE EXPRESSIONS FOR THE BOILING POINT, THE FREEZING POINT AND THE OSMOTIC PRESSURE OF AN IDEAL SOLUTION AND OF THE VARIATION OF LATENT HEAT WITH TEMPERATURE.

By

K. S. GURURAJA DOSS

The derivations of expressions for the boiling point, the freezing point and the osmotic pressure are usually done by working a reversible cycle or with reference to a graph. An alternative (but equally rigorous) proof is suggested herein which does not involve the introduction of a cycle or reference to a graph.

MOLAR ELEVATION OF THE BOILING POINT

The boiling point of a liquid (solution or pure solvent) is the temperature at which the vapour pressure of the liquid equals the atmospheric pressure. Hence, the vapour pressure of any solution at its boiling point equals the vapour pressure of the solvent at its boiling point. One can therefore define the molar elevation of boiling point by the partial differential $\left(\frac{\delta T}{\delta x}\right)_p$, where T is the temperature of the solution, x the mole fraction of the solute and p the vapour pressure of the solution. From the well-known properties of partial differentials, we get,

$$\left(\frac{\delta T}{\delta x}\right)_p = -\frac{\left(\frac{\delta p}{\delta x}\right)_T}{\left(\frac{\delta p}{\delta T}\right)_x} \qquad (1)$$

Raoult's law for the lowering of vapour pressure can be put in the form

$$\left(\frac{\delta p}{\delta x}\right)_T = -p_0 \qquad (2)$$

where p_0 is the vapour pressure of the pure solvent.

The Clausius-Clapeyron equation gives the result

$$\frac{d \ln p_o}{dT} = \frac{\Delta H}{RT^2}$$

$$\text{or} \quad \frac{dp_o}{dT} = \frac{\Delta H}{RT^2}\, p_o \tag{3}$$

At small concentrations of a non-volatile solute, equation (3) may be expected to hold also for solutions. Combining (1), (2) and (3), we get.

$$\left(\frac{\delta T}{\delta x}\right)_p = - \frac{-p_o}{\frac{\Delta H}{RT^2} \cdot p_o} = \frac{RT^2}{\Delta H}$$

which is the required expression.

MOLAR DEPRESSION OF THE FREEZING POINT

The freezing point of a liquid (solution or pure solvent) is the temperature at which the liquid phase and the solid phase have the same vapour pressure. Thus the difference between the vapour pressures of the solid and liquid phases at the freezing point of a solution equals the difference between the vapour pressures of the solid and liquid phases of the pure solvent at its freezing point. (In fact, both of the quantities are equal to zero). The molar depression of freezing point can therefore be defined by the partial differential,

$$\left(\frac{\delta T}{\delta x}\right)_{p_l - p_s}$$

where p_l is the vapour pressure of the liquid phase and p_s is the vapour pressure of the solid phase.

Now,

$$\left(\frac{\delta T}{\delta x}\right)_{p_l - p_s} = - \frac{\left[\frac{\delta(p_l - p_s)}{\delta x}\right]_T}{\left[\frac{\delta(p_l - p_s)}{\delta T}\right]_x}$$

$$\frac{\left(\frac{\delta p_l}{\delta x}\right)_T - \left(\frac{\delta p_s}{\delta x}\right)_T}{\left(\frac{\delta p_l}{\delta T}\right)_x - \left(\frac{\delta p_s}{\delta T}\right)_x} \tag{4}$$

From the Raoult's Law,

$$\left(\frac{\delta p_l}{\delta x}\right)_T = -p_o \tag{5}$$

If the solid phase is pure solvent,

$$\left(\frac{\delta p_s}{\delta x}\right)_T = 0 \tag{6}$$

From Clausius—Clapeyron equation,

$$\left(\frac{\delta p_l}{\delta T}\right)_x = \frac{\Delta H_{l\rightarrow v}}{RT^2}\, p_o \tag{7}$$

$$\text{and } \left(\frac{\delta p_s}{\delta T}\right)_x = \frac{\Delta H_{s\rightarrow v}}{RT^2}\, p_o \tag{8}$$

where $\Delta H_{l\rightarrow v}$ is the latent heat of vapourisation of the liquid solvent and $\Delta H_{s\rightarrow v}$ is the latent heat of vapourisation of the solid solvent,

Combining equations 4, 5, 6, 7 and 8, we get,

$$\left(\frac{\delta T}{\delta x}\right)_{p_l - p_s} = -\frac{-p_o}{p_o \dfrac{\Delta H_{l\rightarrow v} - \Delta H_{s\rightarrow v}}{RT^2}}$$

$$= -\frac{RT^2}{\Delta H_{s\rightarrow l}}$$

where $\Delta H_{s\rightarrow l}$ is the latent heat of fusion. The minus sign indicates that the freezing point is lowered by an increase in the mole fraction of the solute.

OSMOTIC PRESSURE

Callendar's mechanism of osmotic pressure tells us that the phenomenon of osmosis is to be attributed to the difference in vapour pressures of the solution and the solvent on the two side of the membrane. The osmosis can be prevented by a definite hydrostatic pressure as it thereby renders the vapour pressure of the solution equal to that of the solvent. Thus, one can express the osmotic pressure of solution per mole of the solute by the partial differential

$$\left(\frac{\delta p_h}{\delta x}\right)_{p_v}$$

where p_h is the hydrostatic pressure on the solution side and p_v is the vapour pressure of the solution. Now,

$$\left(\frac{\delta p_h}{\delta x}\right)_{p_v} = -\frac{\left(\dfrac{\delta p_v}{\delta x}\right)_{p_h}}{\left(\dfrac{\delta p_v}{\delta p_h}\right)_x} \tag{9}$$

From Raoult's law,

$$\left(\frac{\delta p_v}{\delta x}\right)_{p_h} = -p_o \qquad (10)$$

It can be shown thermodynamically that

$$\frac{\delta p_v}{\delta p_h} = \frac{V_l}{V_v} \cong \frac{V_l p_o}{RT}$$

where V_l & V_v are the molar volumes of liquid and vapour respectively.

Combining equations 9, 10 & 11, we get,

$$\left(\frac{\delta p_h}{\delta x}\right)_{p_v} = -\frac{p_o}{\frac{V_l p_o}{RT}} = \frac{RT}{V_l}$$

For small values of x,

$$p_h = \frac{x}{V_l} \cdot RT = CRT$$

which is the expression required.

The variation of latent heat (of fusion or vaporisation) with temperature.

The variation of latent heat with temperature can be expressed by the partial differential. $\left(\frac{\delta \Delta H}{\delta T}\right)_{eq}$, the suffix "eq" referring to the fact that the quantity is measured under equilibrium conditions. Now,

$$\left(\frac{\delta \Delta H}{\delta T}\right)_{eq} = \left(\frac{\delta \Delta H}{\delta T}\right)_p + \left(\frac{\delta \Delta H}{\delta p}\right)_T \left(\frac{\delta p}{\delta T}\right)_{eq}$$

$$= \Delta C_p + \frac{\Delta H}{T\Delta V}\left\{ \Delta V - T\left(\frac{\delta \Delta V}{\delta T}\right)_p \right\}$$

$$= \Delta C_p + \frac{\Delta H}{T} - \frac{\Delta H}{T}\left\{ \frac{\delta \ln \Delta V}{\delta \ln T} \right\}_p$$

For vaporisation (if the boiling point is far removed from critical temperature),

$$\left(\frac{\delta \ln \Delta V}{\delta \ln T}\right)_p \cong \left(\frac{\delta \ln \Delta V_v}{\delta \ln T}\right)_p = 1$$

since V_v, the molar volume of the vapour is large and the vapour obeys the gas laws.

$$\therefore \left(\frac{\delta \Delta H}{\delta T}\right)_{eq} = \Delta C_p. \quad \text{[For vaporisation]}$$

For fusion (as ΔV is small),

$$\left(\frac{\delta\, ln\, \Delta V}{\delta\, ln\, T}\right)_p \text{ is negligible.}$$

Hence,

$$\left(\frac{\delta \Delta H}{\delta T}\right)_{eq} = \Delta C_p + \frac{\Delta H}{T} \quad \text{[For fusion]}$$

This method is applicable to several other derivations. It brings out clearly all the assumptions underlying the derivation. It is rigorous and hence leads to the correct results.

SUMMARY

Simple analytical derivations have been suggested for the expressions relating to the boiling point, the freezing point and osmotic pressure of ideal solutions and for the variation of latent heat with temperature. The method of derivation is rigorous and brings out clearly all the underlying assumptions.

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THE SPACE GROUP DETERMINATION OF THE CRYSTALS OF p-AZOTOLUENE

By

MATA PRASAD AND M. R. KAPADIA

Crystals of p-azotoluene were prepared by the slow evaporation of the solution of the substance in acetone. The prominent faces developed are (001) and (100), and the crystals belong to the monoclinic prismatic class. The axial ratio are

$$a : b : c :: 2{\cdot}1768 : 1 : 1{\cdot}9674;\ \beta=90^\circ16'.$$

(cf. Chem. Krystal. Groth, Vol. V, p. 66.)

Rotation photographs taken about a, b, and c axes, using copper anticathode, (cf. Plates I, II, and III,) gave the following axial lengths :—

$$a=12{\cdot}00\mathring{A},\ b=4{\cdot}851\mathring{A},\ c=9{\cdot}703\mathring{A}.$$

Thus, $a : b : c=2{\cdot}474 : 1 : 2{\cdot}000$

It will be noticed that the ratio b : c found by the authors agrees fairly well with that given in Groth. The ratio a : b, however, shows considerable difference. On referring to Groth it will be seen that interfacial angles measured by different observers do not agree with each other.

From the axial ratio obtained by the authors the various interfacial angles are calculated on the assumption that $\beta=90^\circ19'$ (Groth's determination), and they are put side by side with those observed by Billows and Groth. The axial ratio given in Groth (Vol.V) is calculated from the measurements made by Billows.

	Billows' observed	Groth's observed	Calculated from the cell dimensions given above
100 : 001	89°44'	89°41'	89°41'
$11\bar{1}$: 100	67°50'	69°56'	69°58'
$\bar{1}11$: 001	65°18'	94°46'	64°59'
$11\bar{1}$: $\bar{1}11$	68°32'	65°48'	65°36'

It is quite clear from these values that our observations agree almost completely with those of Groth, and therefore, the axial ratio determined from the angular measurements of Groth would be very nearly the same as ours. We have also noticed the observations of Zepharovich (Groth, vol. V, p. 66), who finds the angle between $20\bar{1}$: 100 to be 32°0'. This angle calculated from the axial ratio found by us comes to be 31°57'(β taken to be equal to 90°45', as taken by Zepharovich), in very good agreement with the observed value.

Oscillation photographs were taken about all the three axes at intervals of 15° and were worked out by the aid of Bernal's chart. The list of planes observed is given in Tables I and II. The intensities of the planes were determined by eye estimation and the symbols used have the usual meaning.

TABLE I.

Axial Planes.	Prism Planes. okl	Prism Planes. hol	Prism Planes. hko
001 v.s.	011 v.w.	201 v.s.	110 v.s.
002 s.	012 v.s.	202 m.	120 w.
003 w.	013 s.	203 s.	210 s.
004 w.	015 v.w.	204 m.s.	220 v.w.
200 v.s.	023 w.m.	205 w.	310 w.m.
400 m.s.		$20\bar{1}$ v.s.	320 m.
600 m.s.		$20\bar{4}$ w.	410 w.m
020 w.m.		401 m.	420 m.
		402 m.	510 m.s.
		404 m.s.	520 w.m.
		$40\bar{1}$ v.s.	610 m.
		$40\bar{2}$ v.w.	
		601 w.	
		603 v.w.	
		$60\bar{1}$ v.w.	
		$60\bar{2}$ m.	

TABLE II.

General planes

111 m.s.	211 s.	311 v.s.	$41\bar{4}$ w.
112 v.s.	212 w.	812 m.s.	421 w.m.
113 s.	213 m.s.	313 m.	422 w.m.
114 m.s.	214 m.s.	314 m.s.	423 v.w
115 m.	215 w.	$31\bar{1}$ v.s.	$42\bar{1}$ w.
121 v.w.	$21\bar{1}$ v.s.	$31\bar{2}$ m.	$42\bar{2}$ w.m.
122 s.	$21\bar{2}$ vs.	$31\bar{3}$ m,s.	$42\bar{3}$ w.
123 m	$21\bar{3}$ ms.	$31\bar{4}$ s.	511 w.
$11\bar{1}$ v.s.	$21\bar{4}$ s.	322 w.m.	512 m.
$11\bar{2}$ v.s,	$21\bar{5}$ v.w.	323 m.	513 w.
$11\bar{3}$ m.s.	221 w.	324 w.	$51\bar{1}$ w.
$11\bar{4}$ v.w.	222 m.	$32\bar{2}$ m.	$51\bar{2}$ m.
$11\bar{5}$ v.w.	223 m.	$32\bar{3}$ m.	$51\bar{3}$ w.m.
$12\bar{1}$ v.w.	224 w.	411 m.s.	611 v.w.
$12\bar{2}$ s.	$22\bar{2}$ m.s.	412 m.s.	612 v.w.
$12\bar{3}$ w.	$22\bar{3}$ m.s.	$41\bar{1}$ m.	613 v.w
$12\bar{4}$ m.	$22\bar{4}$ m.	$41\bar{2}$ m.	$61\bar{2}$ w.m.

It will be noticed that the planes (hol) are halved if h is odd, and (010) is also halved. These halvings correspond to the space group C^5_{2h}. The number of molecules in the unit cell calculated from the density of the crystals and the dimensions of the unit cell is two, which is half the number required by the space group. This shows that there is a centre of symmetry in the molecules.

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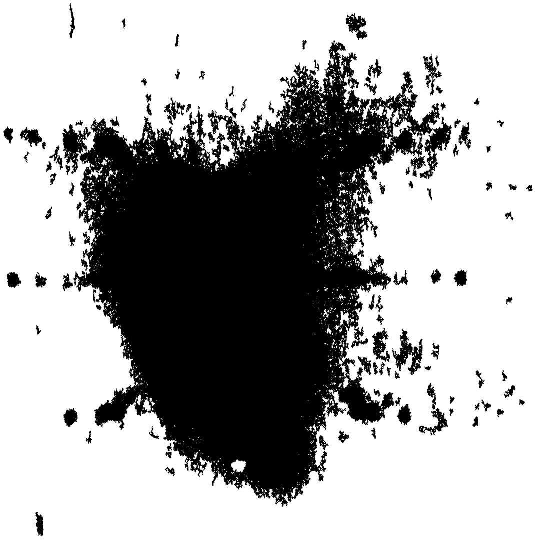
1 Rotation photograph about *a* axis



2. Rotation photograph about *b* axis

3 Rotation photograph about *c* axis.

DIELECTRIC PROPERTIES OF GLYCERIDES
PART I

By

B. V. BHIDE and R. D. BHIDE

The property of exhibiting a double melting point has long been regarded as a characteristic of nearly all mono, di, and tri-glycerides. Several observers have recorded that these glycerides melt at a certain temperature, solidify at a higher temperature and melt again on further heating. This phenomenon has been studied by previous workers by thermal investigation. Joglekar and Watson (J. Ind. Inst. Sc., 1930, *13A*, 121) found two forms of tristearin, one form melting at 71.8° and another form melting at 55°. Clarkson and Malkin (J. Chem. Soc. 1934, 666) confirmed the results of Joglekar and Watson and they called the form melting at 71·8° (obtained by crystallisation from a solvent), the β form. This form is the stable form. The other form melting at 55° is a glass. This form is obtained by cooling the melt of the β form. On heating the glass above its melting point, it is transformed again into an unstable α form melting at 65° which changes finally into the β form melting at 71.8°.

M. M. Ramrao and Kulkarni (J. Ind. Chem. Soc. 1935, *12*, 574) measured the heats of transition of these forms by determining the heats of solutions of the two forms in different solvents. They concluded that in solution the stable form is present. It appeared that more light on the question may be obtained by the study of the dielectric constants of these glycerides, particularly because these are highly polar substances. Investigations of this type have already been carried out by several workers (Buckingham, Trans. Far. Soc. 1937, *30*, 377; White and Morgam, J. Chem. Phys. 1934, *5*, 377; Smyth and Baker, *Ibid.* 666 etc.). In this paper the investigation of tristearin is described.

EXPERIMENTAL

Apparatus :—Dielectric constants were measured by the resonance method at two different frequencies, (930 Kc/s and 4400 Kc/s). After a number of trials the following circuit was adopted. The oscillator was of the reaction type (Fig. 1). The coils were of the plug in type so that the same circuit could be used for two different frequencies. The Valve was Phillips T. C. 03/51 with 200 volts on the plate; the normal plate current was 50 milliamperes.

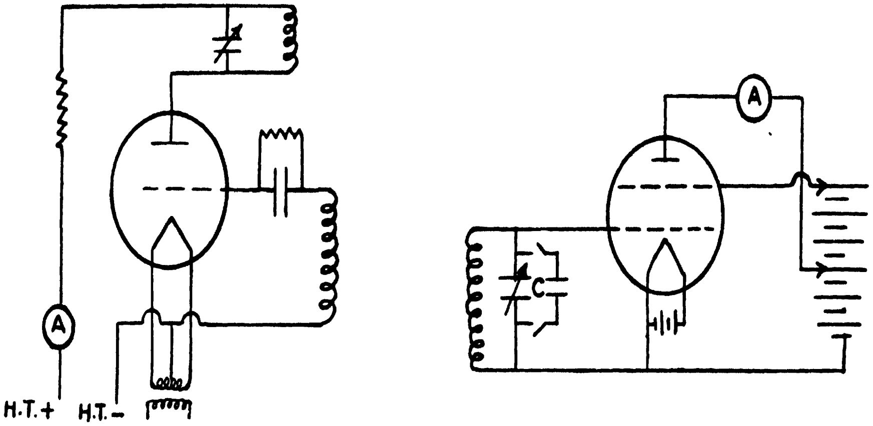


Fig. 1.

The resonant circuit consisted of an inductance capacity circuit connected between the filament and the grid of a screen grid valve (Phillips A 442) which worked in its dynatron position. The variable condenser C in the wave-meter circuit was a precision condenser (500 $\mu\mu$ F, type 722-F General Radio Co.) on which 0.1 $\mu\mu$ F could be read directly. The plate voltage was 6 and the screen had 18 volts. The oscillator was quite powerful and free from harmonics. The experimental condenser consisted of two concentric brass cylinders silver plated, carefully insulated from one another by a tight ebonite top. The top had two holes through which a thermometer and the substance could be inserted. The condenser was placed in a Dewar flask filled with paraffin. The bath was electrically heated and stirred by small motor stirrer. The temperature was controlled by regulating a rheostat placed in the heating circuit.

Benzene was used for standardising the apparatus so as to eliminate the capacity of leads etc. Accuracy of the instrument was checked by determining the dielectric constants of chloroform and carbon tetrachloride. The results agreed well with the values obtained by Davies (Phil. Mag., 1936, *21*, 1).

The accurate determination of the dielectric constants of solids is an exceedingly difficult matter. If a solid is cooled between the two plates of condenser, contraction takes place on cooling and voids are formed. These do not necessarily possess geometrical dimensions and hence the correction for these voids is bound to be uncertain (*Vide* Buckingham. Loc. cit.). However, the number of molecules between the plates remains the same and hence the results obtained are quite comparable, although the true dielectric constant may be even 20 per cent. higher than the values mentioned in this paper. To test this point and also to determine whether reproducible results could be obtained for solids, a number of measurements were carried out with benzophenone. The values for liquid benzophenone are in complete agreement with the values of MacNeight and Smyth (J. Am. Chem. Soc.·1936, *58*, 1718).

Benzophenone was obtained from Merck and was recrystallised before use. It melted at 47·5°. A weighed quantity of benzophenone sufficient to leave a layer, 1 cm. deep, on the inner cylinder of the condenser was introduced and the dielectric constants measured. The values did not differ for solid benzophenone during several experiments by more than 1 per cent. The values are given in table I.

TABLE I

Frequency=930 Kc./s		Frequency=4400 Kc/s	
Temperature	Dielectric constant	Temperature	Dielectric constant
12·0	3·068	13·5	3·149
15·0	3·068	14·6	3·150
19·1	3·068	15·8	3·153
23·7	3·069	17·6	3·155
26·8	3·073	19·6	3·159
30·9	3·073	21·9	3·166
34·6	3·089	24·7	3·176
39·1	3·12	27·1	3·180
43·0	3·22	28·9	3·183
45·6	3·42	31·3	3·195

TABLE I—*concld.*

melts at 47·4		34·9	3·204
48·9	11·37	38·7	3·215
50·2	11·29	42·8	3·313
52·5	11·25	44·2	3·431
55·8	11·18	46·8	3·787
59·3	11·09	melts at 47·4	
62·5	11·04	49·2	12·63
		50·9	12·50
		54·4	12·32
		58·3	12·27
		62·1	12·18
		65·4	12·12

The values obtained at high frequency are higher than at lower frequency. Smyth working during the frequency range 0·3 to 70 Kc/s observed that the dielectric constant decreases with increase in frequency. This point is under investigation. Near the melting point of the solid the dielectric constant shows rapid rise indicating rotation of the molecules. Below 40° the dielectric constant does not change with temperature at all, indicating the absence of such freedom. The dielectric constant of the liquid falls with rise in temperature in accordance with the results of Smyth.

TRISTEARIN

Tristearin was prepared by the method of Clarkson and Malkin (loc. cit.). About 20 crystallisations were necessary before the pure product could be obtained. It melted at 71·5°.

Experiment I

The substance was heated to 90° in the experimental condenser and allowed to cool gradually and the dielectric constants were measured at different temperatures. It solidified at 55° forming the glass and the α form.

TABLE II

Frequency	930 Kc/s.	Frequency	4400 Kc/s.
Temperature	Dielectric constant	Temperature	Dielectric constant
90·5	2·76	82·5	2·95
88·9	2·77	78·3	2·96
83·6	2·78	73·5	2·97
79·6	2·78	70·7	2·98
77·2	2·79	67·6	2·99
75·2	2·79	64·8	3·00
68·0	2·80	62·1	3·00
64·3	2·81	59·1	3·01
59·8	2·81	57·0	3·02
56·8	2·82	solidification at 55°	
solidification at 55°		54·5	2·87
54·9	2·71	52·8	2·83
53·3	2·68	50·6	2·80
50·5	2·63	46·8	2·76
46·7	2·59	40·6	2·73
43·5	2·56	37·0	2·72
40·4	2·54	28·2	2·67
36·3	2·52	27·5	2·67
34·2	2·51		
27·6	2·50		

Experiment II

The substance in expt. 1 was allowed to stand for two days and dielectric constants were measured when it was gradually heated. It melted at 71·5°.

TABLE III

Frequency	930 Kc/s.	Frequency	4400 Kc/s.
Temperature	Dielectric constant	Temperature	Dielectric constant
27.4	2.50	23.4	2.57
30.6	2.50	30.1	2.59
34.8	2.51	36.2	2.61
38.7	2.52	42.0	2.64
43.9	2.54	46.2	2.66
49.1	2.56	51.3	2.69
52.5	2.57	54.5	2.71
56.6	2.58	55.8	2.72
60.7	2.59	57.6	2.73
64.9	2.61	60.3	2.75
67.6	2.64	62.2	2.76
70.3	2.70	66.3	2.79
melts at 71.5°		68.1	2.81
72.2	2.79	70.4	2.86
73.4	2.79	melts at 71.5°	
75.2	2.79	72.1	2.97
79.8	2.78	73.0	2.97
83.3	2.78	75.5	2.96

Experiment III

The substance was heated to 90° and maintained at that temperature for some time and then rapidly cooled in a mixture of ice and salt. Dielectric constants of this form were measured at different temperatures, as it was gradually heated. It melted at 66°. Crystals of the stable form were introduced at this stage and the temperature was maintained above 60° for about 4 to 5 hours till it completely solidified. The temperature was then gradually raised when the substance melted at 71·5°.

TABLE IV

Frequency	930 Kc/s.	Frequency	4400 Kc/s.
Temperature	Dielectric constant	Temperature	Dielectric constant
24·3	2·67	24·2	2·77
27·5	2·70	28·3	2·81
30·8	2·70	32·0	2·83
35·0	2·72	35·3	2·87
38·3	2·73	41·4	2·90
40·9	2·73	46·2	2·92
44·4	2·74	50·8	2·95
47·4	2·75	54·0	2·96
52·0	2·77	55·1	2·97
55·4	2·78	56·2	2·96
57·3	2·77	59·8	2·90
59·7	2·76	61·5	2·79
62·7	2·72	63·0	2·66
64·7	2·68	65·2	2·65
it melted at 66°		it melted at 66°	
67·0	2·81	67·8	2·99
68·3	2·80	crystals of β form introduced.	
crystals of β form introduced.			
61·0	2·48	61·3	2·47
63·0	2·49	63·8	2·48
66·5	2·51	66·5	4·50
68·1	2·52	70·2	2·55
70·2	2·56	melted at 71·5	
melted at 71·5			
72·1	2·80	72·7	2·97
73·2	2·79	75·5	2·98
75·8	2·79	79·1	2·96

Experiment IV.

The substance was heated to 90°, cooled down to 68° and crystals of the stable β form were introduced and the temperature maintained till the tristearin solidified. It was gradually allowed to cool and the dielectric constants were measured at different temperatures. This solid on heating melted at 71·5°.

TABLE V.

Frequency	930 Kc/s.	Frequency	4400 Kc/s.
Temperature	Dielectric constants	Temperature	Dielectric constants
76·5	2·78		
70·3	2·80	74·8	2·97
78·0	2·81	73·5	2·97
crystals of the β form introduced.		72·5	2·98
		69·0	2·98
67·2	2·51	crystals of β form introduced at 68	
64·4	2·49	67·7	2·52
62·5	2·48	65·5	2·50
60·2	2·47	63·8	2·49
57·9	2·46	61·3	2·48
56·1	2·45	58·8	2·47
55·1	2·45	55·0	2·47
54·0	2·45	42·0	2·46
48·3	2·44	29·0	2·46
42·4	2·43		
36·0	2·42		
31·0	2·42		

DISCUSSION OF RESULTS.

Curves given in figs. 2 and 3 represent the dielectric constants at different temperatures measured at 930 Kc/s and 4400 Kc/s respectively. The two sets of observations emphasise the fact that the general nature of the curves is the same even when the dielectric constants are determined at such widely different frequencies. Curve I (Fig. 2) shows the variation of the dielectric constant when the melted tristearin is gradually cooled. The sudden fall in the dielectric constant at 55° indicates solidification. Curve III represents the dielectric constants of the stable β form melting at 71·5°. Clarkson and Malkin from an X-ray investigation find that the long chain acid component is rotating round the oxygen linkage and this freedom is absent in the β form. If such rotation is absent the dielectric constant should be low. Actually the values obtained are lower than those obtained for any other form. Thus support is obtained for the presence of rotating chains in the glass and α

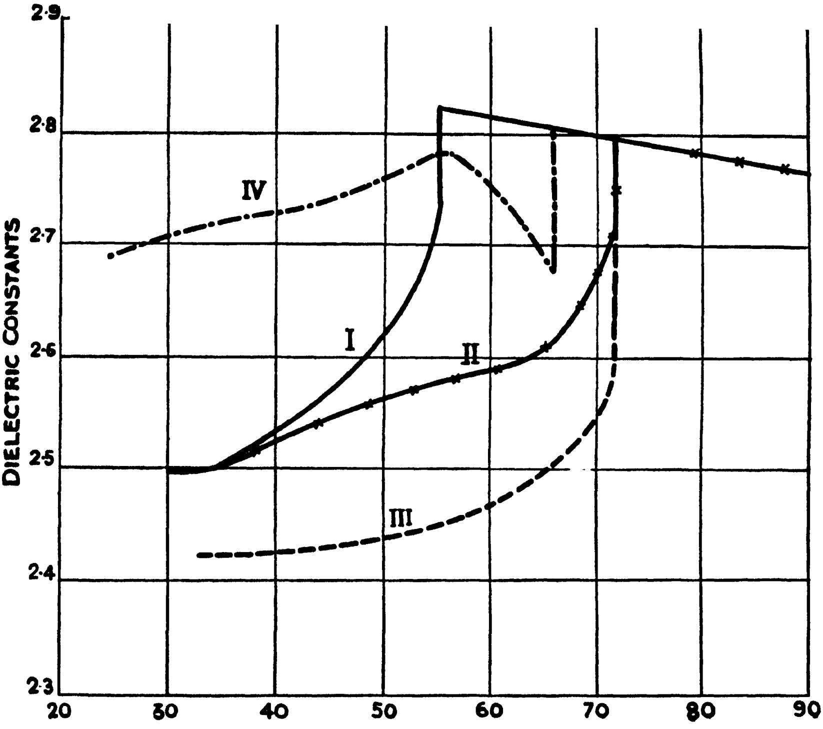


Fig. 2.

form. Curve IV gives the dielectric constants of the glass which as expected has values similar to that of the liquid. The values however, are smaller than those which could be obtained by intrapolation from the dielectric constants of the liquid. These low values can be attributed to two reasons. During solidification of the liquid, due to contraction, voids are formed and these might account for the low values. Secondly, since about 4-5 hours are required for the experiment, transformation into the α and β forms might take place. The curve shows a maximum at 55° showing the transformation of the glass into the α form which melts at 66° (65° Malkin). An accurate value of the dielectric constant for the α form cannot be obtained on account of the ease with which it is transformed into the β form. The nature of the α form is very complex. To detemine the dielectric constant of the glass the substance was melted and chilled in a mixture of ice and salt and immediately introduced into a bath maintained at 54° and the dielectric constant measured; the value was 2·79 at 930 Kc/s and 2·98 at 4400 Kc/s. The values are nearly those of the liquid.

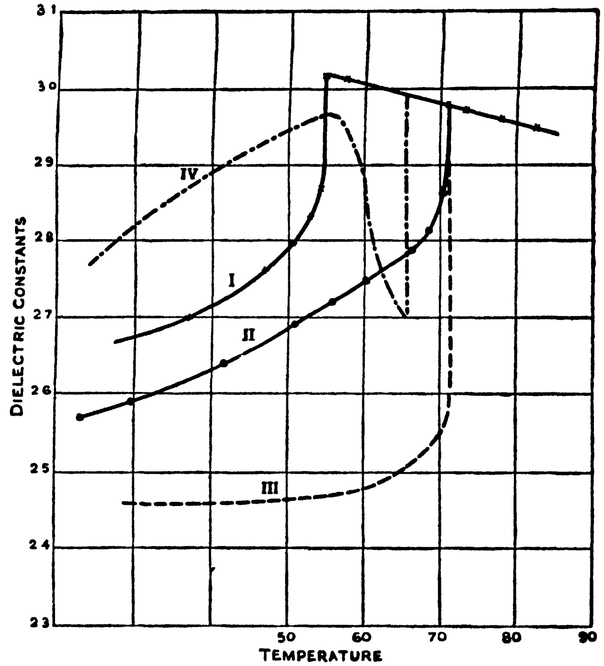


Fig. 3.

Curve II indicates the dielectric constants of the substance kept for two days after gradual solidification. The dielectric constant observed is higher than that for the pure β form. This shows that the transformation of α form into β form is slow at room temperature. Although the melting point of the substance is $71 \cdot 5^{\circ}$ the dielectric constant shows it to be not the pure β form. The dielectric constant appears to be more reliable than the melting point in determining the purity of the β form.

Other glycerides are being investigated in this laboratory on similar lines. One of us (B.V.B) wishes to thank the University of Bombay for the grant which defrayed part of the cost of the apparatus used in these experiments.

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KINETICS OF REACTIONS IN HETEROGENEOUS SYSTEMS

Part III.—Hydrolysis of Acid Halides with Water.

By

DINAKAR KARVE AND KRISHNAJI KHANDO DOLE

In continuation of the study of the reaction between carbon disulphide and alkali and the reaction between benzoyl chloride and water in heterogeneous systems (cf. Karve and Dole, J. Indian Chem. Soc. 1935 *12*, 719–739), hydrolysis of acid halides has been investigated. In the previous investigation (loc. cit.) the liquid-liquid heterogeneous systems were roughly classified as (i) homo-heterogeneous and (ii) purely heterogeneous ones. The hydrolysis of acid halides dissolved in monochlorbenzene by water are reactions of the second type. The study of the homo-heterogeneous reactions is complicated by the mutual solubility of the reactants in the two phases and therefore no universally applicable formula has been yet found for such reactions. The purely heterogeneous reactions may be cosidered to be analogous to the reactions in solid-liquid systems, in which the reactions take place at the surface of contact of the two phases and the velocity of the reactions is determined by the speed of diffusion of the reactants and the reaction products to and from the surface of contact, respectively.

Three important views have so far been put forward to explain the heterogeneous reactions in solid-liquid systems. (i) The modified Noyes-Whitney-Nernst theory of 'Diffusion layer'. (Zeit. physikal. Chem. 1897, *23*, 689-692; 1904, *47*, 52). According to this theory a saturated layer of reaction products is formed at the surface of contact and the velocity of reaction depends upon the diffusion of the reaction products from this layer into the surrounding medium. Nernst assumed that all chemical reactions are fairly rapid as compared with the diffusion processes and therefore the diffusion processes govern the reaction velocity. But this assumption is no longer true. There are various heterogeneous reactions in which the chemical process is slower than the diffusion process, in which case the reaction velocity is determind by the former.

The diffusion layer theory has been severely criticized by Ericson-Auren (Zeit. anorg. Chem., 1898, *18*, 83 ; 1901, *27*, 209 ;

Wildermann (Zeit. physikal. Chem., 1909, *66*, 445); Roller (J. Phys. Chem. 1931, *35*, 1133; 1932, *36*, 1202; 1935, *39*, 221), and by Palmaer (Zeit. physikal. Chem., 1906, *56*, 689). Wildermann claims that the assumption of a diffusion layer is unnecessary, since, the same velocity equations can be derived without its use. He further showed that the diffusion layer theory cannot explain the dependence of the velocity of solution of gypsum on the physical properties of the material and variation with different faces of the crystals. In order to explain these facts the 'Adsorption layer' theory has been advocated.

This theory has also been advocated by Bell (J. Phys. Chem., 1928, *32*, 882-893,) for liquid-liquid systems. He assumes that an adsorbed film of benzoyl o-toluidide on which the permanganate ions strike, brings about the reaction. But this theory is not supported by Kassel and Schaffer (J. Amer. Chem. Soc., 1929, *51*, 965) who repeated the same work next year.

In the opinion of Roller there is no necessity of the assumption of either a diffusion layer or an adsorption layer. The reactions can be explained on the basis of known physical and chemical laws.

Recently King (J. Amer. Chem. Soc., 1935 *57*, 828-831,) has attempted to answer the criticism on Nernst's theory by slightly modifying the conceptions of the 'diffusion layer'. According to him there is no sharply defined adhering layer and the thickness of the layer varies with the speed of stirring and diffussion coefficient of the reagents.

In the present investigation the reactions are predominently heterogeneous and the homogeneous part is negligible. Therefore, for all practical purposes they can be considered as heterogeneous reactions.

Experimental

The reactants were mixed in conical flasks of 250 c.c. capacity stoppered with clean corks. Rubber stoppers were avoided since organic solvents were used in the experiments. 10·0 c.c. of the solution of the acid halide were added to 50·0 c.c. of pure water or the solution used. The flasks were then quickly attached to a shaking machine of the ordinary bottle-shaker type, giving horizontal to and fro motion to the flasks, which were held vertically in the machine. After shaking for definite periods at a known speed the flasks were removed from the machine and their contents poured into separating funnels. The upper aqueous layer was then used for the estimation of the extent of hydrolysis.

In most of the experiments monochlorbenzene was used as solvent for the acid halides. The considerations which governed the choice of the solvent were that it (1) was inert, (2) was immiscible with water, (3) had a specific gravity not very different from that of water, (4) formed no emulsion with water, (5) was non-volatile, (6) had low interfacial tension and viscosity and (7) dissolved both the acid halide and, in most cases, the aromatic acid formed. On account of its specific gravity and interfacial tension it gave uniform and reproducible results under different conditions. It was suitable with benzoyl chloride upto 1·0 N solutions. But with other acid halides it was found unsuitable since the solubility of the substituted aromatic acids in it was not adequate. The difficulty was partly got over by using low concentrations of the acid halides. All the common solvents like chloroform, carbon-tetrachloride, nitrobenzene, brombenzene, bromoform, benzene, toluene, xylene and petroleum were equally unsuitable for the purpose on the same grounds. It is possible that mixed solvants may prove better suited.

The experiments were performed at a constant temperature of $30^\circ \pm 0{\cdot}05$ in an air thermostat.

Control of Speed:— The speed of the electro-motor used for the shaking machine, was controlled by introducing a suitable rheostat, regulated by hand. The actual revolutions per minute were counted by a revolution counter and a stop-watch. On account of the shaky motion of the machine, the pointer of the tachometer was unsteady and failed to give any correct indication. After several trials the use of a stroboscopic disc was found most suitable for the purpose. With a set of suitable pulleys attached to the driving motor a stroboscopic disc was run outside the box. The disc consisted of six black and six white sectors and was lighted by an A. C. lamp of frequency of 50 cycles per second. In this case the disc will appear steady at 1000 r.p.m. according to following equation :—

$$n = \frac{f \times 120}{P};$$

where n is the speed of the disc, f, the frequency of A. C. current, and P, the number of black or white sectors on the disc. The ratios of the circumference of the pulleys were adjusted in such a way that 159 shakes of the shaking machine corresponded to 1000 revolutions of the stroboscopic disc. The fine adjustment of this ratio was made by winding a few turns of a thin strong cotton string of suitable length either to the pulley of the disc or the driving pulley, which were specially made with a flat groove for the purpose.

Choice of Speed :—In our previous investigation it was found in the study of the relation of speed and amount of reaction, that the curve representing this relation rises steeply at first, reaches a maximum and then drops again. With higher speeds of agitation there is actually a decrease in the amount of reaction. Throwing out of the heavier liquid towards the walls of the vessels, due to its violent to and fro movement thus appears to prevent thorough mixing of the two layers and to diminish the surface of contact. Curves with different solvents and with conical flasks of different capacities are found to be slightly different. In case of monochlorbenzone with 250 c. c. flasks the maximum point on the curve corresponds with 158 to 160 r. p. m. indicating that at this speed the agitation was most efficient in giving the maximum reaction, (cf. Karve and Dole, loc. cit., Table No. I, page 735). The gradient of the curve at this point is zero, so that the slight variation of the reaction with slight change of speed., near about this point is negligible, when compared with the variation at the other points on the curve. In the present study, therefore the shaking machine was adjusted so as to run at 159 r. p. m. It may be mentioned here that the flasks used in these experiments were carefully selected and only those giving identical results in the trial experiments were taken.

Method of Estimation :—In the method employed (Lang and Messinger's method, Ber. 1930, *53*, 1429-1431) diphenylamine was used as an absorption indicator, which was freshly prepared for each titration. We found that it was necessary to add one drop of indicator for every 3 c. c. of the decinormal silver nitrate solution required in the titration, When the amount of silver nitrate required is very small, it is very difficult to note the end point, since the precipitate and the upper liquid are dark blue instead of green and the change to violet is not easy to observe. Also, with very large quantities of the precipitate, the upper solution appears white instead of green and the change to violet is not easily seen. The solutions of decinormal strengths could be easily titrated with the indicator but solutions of strenghts above that or lower than half decinormal could not be accurately titrated. Then again, if the resultant volume of the titration mixture was too large (more then 100 c. c.) the indicator was not so accurate. When hydrobromic acid was titrated the quantity of the indicator had to be increased by about one and a half times.

In studying the reactions, 50 c. c. of water was shaken with different solutions of the acid halides, so that water was in large excess. The constants were calculated according to the mono-molecular formula

$$K = \frac{1}{t} \log_e \frac{a}{a-x}$$

Since hydrocarbons like monochlorbenzene and monobrombenzene were used as solvents, the solubility of hydrochloric acid in them was first studied. It was found that hydrogen halides are not soluble in the non-aqueous solvents under the experimental conditions and therefore, the proposed method of estimation was reliable and accurate.

Purification of Substances :—All the reagents like sulphuric acid, potassium dichromate, sodium acetate, sodium sulphate and sodium hydroxide were tested for absence of halides. The acid halides were generally purified by distillation at atmospheric pressure or at low pressures according to individual boiling points. Monochlorbenzene was repeatedly used after purification according to the following method:—The waste monochlorbenzene was collected in flasks and dried over fused calcium chloride. It was afterwards distilled, the distillate being collected over sodium hydroxide. This distilled product was kept over solid sodium hydroxide for a week and redistilled. The redistilled product was tested for absence of soluble halides and then used as solvent.

Wherever it was found suitable, four concentrations of the acid halides were studied. In most of the acid halides higher concentrations could not be studied due to (1) the insolubility of the organic acid produced in the reaction and (2) the introduction of a solid phase into the reaction mixture. The results obtained are given below:—

TABLE I

Hydrolysis of benzoyl chloride

Time in minutes	Values of K 1·0M $C_6H_5.COCl$	Values of K 0.75M C_6H_5COCl	Values of K 0.5M $C_6H_5.COCl$	Values of K 0.25M $C_6H_5.COCl$
15	0.0146	0.0145	0.0129	0.0126
30	0.0165	0.0149	0 0137	0.0128
45	0.0166	0.0149	0.0142	0.0132
60	0 0168	0.0155	0.0143	0.0136
75	0.0168	0.0157	0.0144	0.0136
90	0.0164	0.0148	0.0146	0.0134
*Mean	0.0166	0.0152	0.0142	0.0133

*Mean of last five values.

TABLE II

Hydrolysis of benzoyl bromide.

Time in minutes	Values of K 1.0M C_6H_5. COBr.	Values of K 0.75M C_6H_5COBr.	Values of K 0.5M C_6H_5. COBr.	Values of K 0.25M C_6H_5 COBr.
10	0.0275	0.0291	0.0266	0.0253
20	0.0319	0.0292	0.0269	0.0260
30	0.0304	0.0302	0.0272	0.0262
40	0.0334	0.0304	0.0278	0.0262
50	0.0363	0.0301	0.0276	0.0269
60	...	...	0.0281	0.0257
Mean	0.0318	0.0298	0.0274	0.0260

TABLE III

Hydrolysis of cinnamoyl chloride.

Time in minutes	15	30	45	60	75	90	Mean
0.5 M sol.	0.0148	0.0161	0.0161	0.0163	0.0165	0.0163	0.0163
0.25M sol.	0.0134	0.0143	0.0149	0.0150	0.0149	0.0153	0.0149

TABLE IV

Hydrolysis of phthalyl chloride.

Time in minutes	K with 1.0M C_6H_4. $(COCl)_2$	K with 0.75M C_6H_4. $(COCl)_2$	K with 0.50M C_6H_4. $(COCl)_2$	K with 0.25M C_6H_4. $(COCl)_2$
15	0.0039	0.0039	0.00387	0.00333
30	0.0043	0.0042	0.00395	0.00335
45	0.0046	0.0045	0.00396	0.00339
60	0.0049	0.0048	0.00413	0.00353
75	0.0051	0.0050	0.00426	0.00385
90	0.0053	0.0051	0.00453	0.00396
105			0.00463	0.00396
120			0.00464	0.00399
135			0.00463	0.00406
150			0.00461	0.00408
165			0.00462	0.00405
180			0.00463	0.00411
Mean	0.0047	0.0046	0.00437	0.00380

TABLE V

Hydrolysis of o-chlorbenzoyl chloride.

Time in minutes	K with 1.0 M o-C_6H_4·ClCOCl	K with 0.75 M o-C_6H_4·ClCOCl	K with 0.50 M o-C_6H_4·ClCOCl	K with 0.25 M o-C_6H_4·ClCOCl
15	0.0047	0.00449	0.00418	0.00408
30	0.0058*	0.00433	0.00437	0.00431
45	0.0050	0.00510	0.00482	0.00451
60	0.0046	0.00507*	0.00533	0.00487
75	0.0044	0.00441	0.00549	0.00502
90	0.0040	0.00439	0.00567*	0.00502
105				0.00520
120				0.00521
135				0.00544
150				0.00556
165				0.00563
180				0.00565
Mean			0.00498	0.00504

N. B.:—The mean value of K of the first six readings in the case of 0.25 M solution of o-chloride is 0.00463.

*Solid phase appeared at this stage of the experiment.

TABLE VI

Hydrolysis of m-chlorbenzoyl chloride.

Time in minutes	K with 1.0 M m-$C_6H_4ClCOCl$	K with 0.75 M m-$C_6H_4ClCOCl$	K with 0.5 M m-$C_6H_4ClCOCl$
30	0.000540	0.000530	0.000510
60	0.000540	0.000531	0.000511
90	0.000541	0.000531	0.000513
120	0.000543	0.000532	0.000515
150	0.000544	0.000533	0.000516
180	0.000544	0.000536	0.000517
Mean	0.000542	0.000532	0.000513

TABLE VII

Hydrolysis of o-brombenzoyl chloride.

Time in minutes	15	30	45	60	75	90	Mean
0.5 M sol.	0.00496	0.00506	0.00517	0.00531	0.00540	0.00557	0.00524
0.25 M sol.	0.00470	0.00475	0.00483	0.00490	0.00499	0.00512	0.00488

TABLE VIII

Hydrolysis of o-iodobenzoyl chloride.

Time in minutes	15	30	45	60	75	90	Mean
0.5 M sol.	0.00198	0.00188	0.00186	0.00183	0.00180	0.00179	0.00183
0.25 M sol.	0.00176	0.00162	0.00160	0.00157	0.00153	0.00151	0.00157

TABLE IX

Hydrolysis of o-nitrobenzoyl chloride.

Time in minutes	10	20	30	40	50	60	Mean
0.5 M sol.	0.0199	0.0223	0.0245	0.0264	0.0278	0.0282	0.0248

TABLE X

Hydrolysis of m-nitrobenzoyl chloride.

Time in minutes	K with 1.0 M m-C_6H_4. NO_2COCl	K with 0.75 M m-C_6H_4. NO_2COCl	K with 0.50 M m-C_6H_4. NO_2COCl	K with 0.25 M m-C_6H_4. NO_2COCl
30	0.00235	0.00234	0.00237	0.00239
60	0.00235	0.00238	0.00238	0.00240
90	0.00238	0.00239	0.00239	0.00240
120	0.00240	0.00239	0.00240	0.00241
150	0.00241	0.00240	0.00240	0.00240
160	0.00241	0.00240	0.00240	0.00240
Mean	0.00238	0.00238	0.00239	0.00240

TABLE XI

Hydrolysis of anisoyl chloride.

Time in minutes	15	30	45	60	75	90
0.25 M sol.	0.0102	0.0064	0.0050	0.0049	0.0045	0.0044

Note :—The acid chlorides (1) p-chlorbenzoyl chloride, (2) p-brombenzoyl chloride, (3) p-nitrobenzoyl chloride, (4) 3:5 dinitrobenzoyl chloride, could not be studied in purely liquid-

liquid systems, since the corresponding acids are practically insoluble in both monochlorbenzene and water.

The above results have been summarised in Table XII.

TABLE XII

Acid halide	1.0 M Sol.	0.75M Sol.	0.50M Sol	0.25M Sol.
C_6H_5COCl	0.0166	0.0152	0.0142	0.0133
C_6H_5COBr	0.0318	0.0208	0.0274	0.0260
$C_6H_5CH:CHCOCl$	...	...	0.0163	0.0149
$C_6H_4(COCl)_2$	0.0047	0.0046	0.00437 (0.00412)	0.00380 (0.00357)
o-$C_6H_4ClCOCl$	...	...	0.00498 ...	0.00504 (0.00463)
m-$C_6H_4ClCOCl$	0.000542	0.000532	0.000513	...
p-$C_6H_4ClCOCl$	...	...	...	...
o-$C_6H_4BrCOCl$	...	...	0.00524	0.00488
p-$C_6H_4BrCOCl$	...	...	...	...
o-C_6H_4ICOCl	...	...	0.00183	0.00157
o-$C_6H_4NO_2COCl$	...	...	...	0.0248
m-$C_6H_4NO_2COCl$	0.00238	0.00238	0.00239	0.00240
p-$C_6H_4NO_2COCl$	...	...	...	...
3:5 $C_6H_3(NO_2)_2COCl$	...	...	...	...
p-$C_6H_4OCH_3COCl$	...	...	...	...

Dashes indicate that no accurate quantitative determinations could be made. The numbers in bracket give the mean values of K for the first six readings, while the adjoining numbers give the mean of twelve readings. In cases where the reaction is very slow *e. g.* m-chlorbenzoyl chloride and m-nitrobenzoyl chloride, the mean values of K are retained as they are, for the individual values of K do not differ to any great extent.

If the values of K are arranged in descending order, (only 0·5 M and 0·25 M concetrations of acid halides can be taken for comparison), we get the following order : Benzoyl bromide, o-nitrobenzoyl chloride, cinnamoyl chloride, benzoyl chloride, o-brombenzoyl chloride, o-chlorbenzoyl chloride, phthalyl chloride, m-nitrobenzoyl chloride, o-iodobenzoyl chloride, m-chlorbenzoyl chloride.

It will be seen that with the exception of m-nitrobenzoyl chloride, and o-iodobenzoyl chloride all the acid halides show the following peculiarities :–(1) The values of K in the individual series steadily increase and tend to remain constant after a certain period. With slowly reacting acid halides this is more marked. (2) The mean values of K are not the same with different concentrations of acid halides but increase with an increase in concentration. (3) The value of K for the first reading is always lower than the other readings for all acid chlorides with the exception of o-iodobenzoyl chloride. m-nitrobenzoyl chloride is an exception to (1) and (2) but conforms to (3); o-iodobenzoyl chloride is an exception to (1) and (3) but conforms to (2). The peculiarities noted above appear to be general characteristics of heterogeneous reactions in liquid systems.

Some possible reasons for the rise in the values of K can now be discussed here. (1) A halogen acid is formed during the hydrolysis of the acid halides and this may act as a catalyser and accelarate the reaction to a certain extent. (2) There may be some rise in temperature due to the collision of the phases and to the heat of reaction. (3) The splitting of the phases into small droplets may have some inertia due to the specific gravity, interfacial tension, and the viscosity of the phases and electro capillarity; consequently the droplets formed at the beginning would be larger and would gradually diminish in size during the progress of shaking. (4) There may be some influence of the organic acid formed during the reaction.

EFFECT OF ACID AND SALTS.

The effect of acid was first examined by adding sulphuric acid to the reaction mixture. 50 c. c. of different concentrations of sulphuric acid solutions were used with 0·5 molar solution of phthalyl chloride, instead of distilled water used in the previous experiments.

TABLE XIII

Hydrolysis of phthalyl chloride with addition of sulphuric acid.

Time in minutes	K with water	K with 0·5 N H_2SO_4	K with 1·0 N H_2SO_4	K with 2·0 N H_2SO_4	K with 3·0 N H_2SO_4
15	0·00387	0·00338	0·00387	0·00360	0·00333
30	0·00396	0·00382	0·00396	0·00385	0·00345
45	0·00412	0·00395	0·00416	0·00408	0·30359
60	0·00427	0·00406	0·00427	0·00413	0·00372
75	0 00440	0·00418	0·00440	0·00427	0·00382
90	0·00453	0·00447	0·00459	0·00439	0·00402
Mean	0·00419	0·00398	0·00421	0·00405	0·00366

Two experiments were performed in order to study the influence of hydrochloric acid. Concentrations of the acid higher than about 0.2 N could not be studied on account of the difficulties of accurate estimation. 50 c. c. of 0.098 N and 0.196 N hydrochloric acid were, respectively, used.

TABLE XIV

Time in minutes	15	30	45	60	75	90	Mean
0.098N HCl	0.00201	0.00220	0.00247	0.00260	0.00285	0.00321	0,00256
0.196N HCl	0.00338	0.00363	0.00380	0.00399	0.00414	0.00427	0.00385

It will be seen from table XIII that the values of K with 0.5N sulphuric acid are lower than that obtained in water only. The values increase to a maximum with 1.0 N acid and then decrease as this concentration is further increased. This has been found to be the case in the presence of hydrochloric acid as well. Thus the addition of certain concentration of acids retards the reaction and the accelarating influence if any is very small. It can be concluded that the increment in the value of K is not due to the catalytic action of the acid formed during the reaction. The presence of the acid may in addition to the catalytic action retard (1) the solubility of the acid in the aqueous phase and thereby decrease the homogeneous part of the reaction and (2) the diffusion of the reaction products in the surrounding medium. Consequently, some experiments were performed in the presence of different concentrations of sodium sulphate and sodium acetate. The latter salt was particulary chosen because its presence would not only retard the diffusion process but would prevent, if any, the catalytic action of hydrochloric acid.

The concentration of phthalyl chloride in monochlorbenzene was 0.5 M and the quantity of aqueous salt solutions taken each time was 50.0 c. c. The concentration of benzoyl chloride solution in monochlorbenzene was 1.0 M.

TABLE XV

Hydrolysis of phthalyl chloride with the addition of sodium sulphate and sodium acetate

Time in minutes	K with pure water	K with 0.25 M Na_2SO_4	K with 0.5 M Na_2SO_4	K with 1.0 M Na Ac	K with 0.5 M Na Ac	K with 0.2 M Na Ac
15	0.00387	0.00272	0.00162	0.00170	0.00212	0.00255
30	0.00396	0,00286	0,00184	0.00188	0.00244	0.00339
45	0,00412	0,00289	0.00190	0.00210	0,00284	0.00408
60	0.00427	0.00291	0.00198	0.00221	0.00297	0.00413
75	0.00440	0.00303	0,00210	0.00235	0.00356	0.00435
90	0,00453	0.00316	0,00228	0,00250	0,00378	0.00463
Mean	0.00419	0.00293	0.00195	0.00212	0.00295	0,00386

TABLE XVI

Hydrolysis of benzoyl chloride with addition of sodium sulphate and sodium acetate.

Time in minutes	K with pure water	K with 0.25 M Na_2SO_4	K with 0.5 M Na_2SO_4	K with 1.0 M NaAc
15	0.0154	0.0104	0.0069	0.0092
30	0.0164	0.0117	0.0071	0.0129
45	0.0165	0.0128	0.0086	0.0129
60	0.0169	0.0128	0.0090	0.0132
75	0.0170	0.0129	0.0095	0.0142
90	0 0172	0.0130	0.0102	0.0149
Mean	0.0168	0.0126	0.0086	0.0136

The influence of the addition of sodium sulphate is seen to be as was expected and the diffusion process in the reaction is retarded to a great extent. The effect is seen to vary with the concentration of sodium sulphate. The influence of sodium acetate is less than was expected. It is also seen that the sulphate has a greater influence in reducing the extent of reaction. All the preceeding experiments have proved that the retarding influence of electrolytes is greater than the catalytic influence of the hydrochloric acid liberated during the progress of the reaction. At the same time the reason for the increase in the values of K has not been explained.

LOCAL RISE IN TEMPERATURE

In order to ascertain this, three flasks were filled with 50. c.c. of distilled water. To one of the flasks 10 c.c. of monochlorbenzene, to the second 10 c.c. of 0.5 M solution of phthalyl chloride in monochlorbenzene, and to the third 10 c.c. of 1·0 M solution of benzoyl chloride in monochlorbenzene were added and the flasks were then shaken with the usual speed at 30° for different periods. From time to time the shaking was interrupted and temperatures of the contents of the flasks noted with Beckmann's thermometer.

TABLE XVII

Time in minutes	water-C_6H_5Cl	water-0.5M $C_6H_4(COCl)_2$ Sol.	water-1·0M C_6H_5COCl Sol.
15	3.72	4.24	4.21
30	3.78	4.15	4.32
45	3.80	4.14	4.28
60	4.00	4.08	4.10
90	4.01	4.08	4.02
120	4.01	4.03	4.01

(30° C corresponded to 3.60 degrees on the Beckmann's thermometer).

These results show that the impact of the phases against each other gives a slight rise in temperature as can be seen from the second column, which represents the results of shaking of monochlorbenzene with water in which case there is no chemical reaction. The maximum rise in temperature is 0.41°. After one and a half hour there is an equilibrium between the heat produced by the impact of the two phases and the heat dissipated. During the reactions of the acid chlorides there is also some heat of reaction, which in case of phthalyl chloride sets up the difference of 0.64° in the beginning and gradually sinks to 0.43°. With benzoyl chloride, however, the maximum rise is at 30 minutes' interval, the difference being 0.72° and it falls to 0.41°. This experiment, therefore, shows clearly that an appreciable time is required for the dissipation of the local rise of temperature. But at the same time this experiment gives no explanation regarding the increase in the values of K in individual experiments because this change in temperature is not enough to cause the observed increase in K.

Effect of shaking

In order to test this, the reaction flasks were shaken vigourously by hand (five or six times) before fixing them to the machine, thereby removing the inertia of the splitting of droplets before the reaction began. The time was noted from the beginning of the shaking by hand. This preliminary shaking hy hand gave sufficiently fine droplets from the very start of the reaction.

The Hydrolysis of 0.5 M phthalyl chloride was studied in this manner. All other factors were kept constant.

TABLE XVIII

Time in minutes.	15	30	45	60	75	90	Mean
Values of K	0.00459	0.00459	0.00461	0.00463	0.00464	0.00463	0.00462

The values of K are seen to be fairly constant. The very slight increase in the values is probably due to the slight solubility of phthalyl chloride in the aqueous phase or to the slight catalytic action of the phthalic acid produced in the reaction. If the values of Table IV are compared with the present ones, it will become clear the preliminary shaking has already split the phases into fine that droplets which state is then maintained by the shaking of the machine and no further decrease in the size of the droplets (*i. e.* increase in the surface of contact) takes place. One more point worth noting is that the values of K in this experiment are similar to those obtained after ninety minutes in the experiment in Table IV. This is a further substantiation of the hypothesis.

Another point in these reactions which requires explanation is that the mean values of K with different concentrations vary with the concentrations of the acid halides. The only exception to this observation is the hydrolysis of m-nitrobenzoyl chloride. The values of K in this case remain steady with different concentrations of the acid chloride, and also there is very little increase in the individual series of it. This variation in the values in the case of other acid chlorides may, perhaps, be due to slight solubility of the acid halides in the aqueous phase. Thus a certain amount of reaction may be taking place in the homogeneous system. With higher concentrations of the acid halides, therefore, the homogeneous part will also increase and add up to the heterogeneous part. Since homogeneous reactions are much more rapid than heterogeneous ones, as a rule, it will be clear that the values of K will be affected by the homogeneous part of the reaction. Another possibility is that the organic acid produced in the hydrolysis may exert a catalytic influence.

It is thus proved that the increment in the values of K in the individual series depends upon the mode of splitting of the two phases. This splitting up has some inertia, which depends upon the physical properties of the two phases. The specific gravity, viscosity interfacial tension, and electrocapillarity will determine the size of the droplets, when the phases are shaken in a certain manner at a certain speed. The physical properties of the monochlorbenzene phase will also change with the addition of different acid halides in different concentrations. Also the physical properties of the aqueous phase will change with the addition of salts and acids. It can be observed in the results, that the difference between the first and the last values of K in individual series varies to a certain extent. It was observed that in the case of those acid halides which showed a small difference between the first and the last values of K, the time taken by the monochlorbenzene phase to separate out after the shaking has stopped was longer showing that the droplets were finer. Cinnamoyl chloride, benzoyl chloride, m-nitrobenzoyl chloride and m-chlorbenzoyl chloride showed slow coagulation; while in the hydrolysis of phthalyl chloride with aqueous acids rapid coagulation was observed. The difference between the first and last values of K in the latter was large.

In order to support the conclusion, the hydrolysis of phthalyl chloride dissolved in monobrombenzene was studied. Due to a higher specific gravity and interfacial tension the non-aqueous phase separated out rapidly.

TABLE XIX

Hydrolysis of phthalyl chloride in monobrombenzene.

Time in minutes.	30	60	90	120	150	180	Mean
Values of K	0.00375	0.00396	0.00430	0.00444	0.00461	0.00482	0.00431

Difference between K of first and last reading =0.00107.

Here also the difference between the first and the last values of K is much larger. The mean value of K under identical conditions with monochlorbenzene as solvent for phthalyl chloride is 0.00437. Since the above mentioned difference may also be affected by a slight partition coefficient of the acid chloride between the two phases, no definite proportionality can be established between the time taken for separating out of the phases and the said difference.

EFFECT OF TEMPERATURE.

With a view to gain further insight into the mechanism of the heterogeneous reactions, temperature coefficients of three reactions were studied. Benzoyl chloride was taken as a representative of faster reactions and phthalyl chloride as the representative of slower ones. m-nitrobenzoyl chloride showed a departure from normal results and therefore the temperature coefficient of its hydrolysis was also studied. The values of K were determined at six defferent temperatures at an interval of two degrees each.

TABLE XX

Temperature coefficient of the Hydrolysis of benzoyl chloride.

Time in minutes	K 26°	K 28°	K 30°	K 32°	K 34°	K 36°
15	0.0117	0.0127	0.0146	0.0163	0.0172	0.0197
30	0.0129	0.0142	0.0165	0.0172	0.0182	0.0214
40				0.0173	0.0187	0.0215
45	0.0132	0.0147	0.0166			
50				0.0174	0.0188	0.0216
60	0.0135	0.0147	0.0168	0.0174	0.0190	0.0220
70				0.0177	0.0192	0.0223
75	0.0139	0.0150	0.0168			
90	0.0154	0.0150	0.0164			
Mean	0.0138	0.0147	0.0166	0.0174	0.0188	0.0217

Mean of last five values of K is given in the table. The temperature coefficient is K 36/K 26 = 0.0217/0.138 = 1.57.

TABLE XXI

Temperature coefficient of the hydrolysis of phthalyl chloride.

Time in minutes	K 26°	K 28°	K 30°	K 32°	K 34°	K 36°
15	0.00335	0.00360	0.00387	0.00440	0.00496	0.00553
30	0.00341	0.00370	0.00396	0.00464	0.00531	0.00606
45	0 00342	0.00373	0.00412	0.00470	0.00541	0.00628
60	0.00345	0.00379	0.00427	0.00475	0.00576	0.00640
75	0.00350	0.00383	0.00440	0.00483	0 00585	0.00657
90	0.00351	0.00408	0.00453	0.00509	0.00600	0.00690
Mean	0.00344	0.00379	0.00419	0.00474	0.00555	0.00629

The temperature coefficient is K 36/K 26 = 0.00629/0.00344 = 1.85.

TABLE XXII

Temperature coefficient of the hydrolysis of m-nitrobenzoyl chloride.

Time in minutes	K 26°	K 28°	K 30°	K 32°	K 34°	K 36°
30	0.00165	0.00192	0.00237	0.00280	0.00334	0.00393
60	0.00165	0.00195	0.00238	0.00283	0.00348	0.00419
90	0.00164	0.00200	0.00239	0.00287	0.00350	0.00423
120	0.00166	0.00200	0.00240	0.00291	0.00354	0.00426
150	0.00166	0.00200	0.00240	0.00291	0.00354	0.00428
180	0.00167	0.00200	0.00240	0.00291	0.00356	0.00430
Mean	0.00165	0.00198	0.00239	0.00287	0.00349	0.00420

The temperature coefficient is K 36/K 26 = 0·00420/0·00165 =2.54.

The temperature coefficients of the three reactions are 1.57, 1·85 and 2·54 for benzoyl chloride, phthalyl chloride, and m-nitrobenzoyl chloride, respectively. The usual number for the hydrolysis reactions, catalysed by mineral acids is about 2·5 and numbers given by the present reactions vary within a wide range, indicating that the velocity of reactions depend on some other process than merely the chemical change. Noyes-Whitney-Nernst have already shown that diffusion process influences the reaction velocity to a great extent. Since, the reaction velocity in heterogeneous systems depends both on the diffusion and the chemical processes, the study of the former may throw much light on the mechanism of these reactions. The lowering of working temperatures will also cause a fall in the diffusions. Öhlm (Zeit. physikal. Chem., 1904, *50*, 309; 1910, *70* 378; Medd. Vet Akad, Nobel Inst., 1912, *2*, Nos. 23, 24, 26) has studied the temperature coefficients of the diffusion of electrolytes and non-electrolytes in liquid media. They vary from 1·2 to 1·48 for aqueous solutions. This value is materially less than that of the temperature coefficients of the homogeneous reactions. It is therefore evident, that in the examination of temperature coefficients of the reaction velocities in heterogeneous media the occurrence of low values between 1 and 1·5 indicate that the predominant factor in determining the reactions rate is the velocity of diffusion. On the other hand, high temperature coefficients will point towards the chemical process as the factor determining the rate of reaction.

Brunner and Tolloczko (Zeit. physikal. Chem., 1900, *35*, 283) while amplifying the work of Noyes and Whitney in solid-liquid systems found the temperature coefficients of the order of 1·5 to 1·8 per ten degrees rise, thus indicating the predominance of the diffusion process over the chemical process. In the reactions of benzoyl chloride and phthalyl chloride also the temperature coefficients are 1·57 and 1·85, indicating predominance of diffusion factor. In the case of m-nitrobenzoyl chloride the temperature coefficience is 2·54 indicating that the chemical process determines the velocity of reaction.

The mechanism of heterogeneous liquid-liquid systems can now be summarised in the following words :—Most of the reactions are homo-heterogeneous; those in which the homogeneous part is negligible may, however, be called heterogeneous processes for all practical purposes, *e. g.* the hydrolysis of m-nitrobenzoyl chloride. The homo-heterogeneous systems may be divided into two subdivisions, (a) the reactions in which the homogeneous part predominates such as, the alkaline hydrolysis of ethyl benzoate and isoamyl acetate studied by Kremann (Monatsheftc., 1905, *26*, 315 to 326) and Goldschmidt (Zeit. Electrochem., 1905, *11*, 430-433) ; (b) the reactions in which the heterogeneous part predominates, such as, the hydrolysis of acid halides studied in this investigation. The modified Noyes-Whitney-Nernst theory is applicable to the liquid-liquid systems. The agitation of the reaction flasks splits up the phases into droplets. Each droplet behaves as a separate entity and the reaction takes place at the surface of the droplets. A layer of the reaction products is formed round each droplet and the reaction velocity is governed by the velocity of the chemical process and that of the diffusion of the reaction products from this layer into the surrounding medium. If the diffusion process is slower than the chemical process then the reaction velocity is governed by the diffusion process, as in the case of hydrolysis of benzoyl chloride, benzoyl bromide etc. If the chemical process is slower of the two, it governs the velocity of reaction, as in the case of m-mitrobenzoyl chloride.

SUMMARY

(1) Hydrolysis of some aromatic acid halides in liquid-liquid heterogeneous systems has been studied. Influence of electrolytes on such systems has been investigated. Temperature coefficients of three typical reactions have been worked out.

(2) An attempt has been made to explain the mechanism of these systems on the basis of the modified Noyes-Whitney-Nernst theory of heterogeneous reactions.

Further work on heterogeneous liquid-liquid reactions is in progress and will be published later. One of the authors (K. K. Dole) gratefully acknowledges the help received from the University of Bombay in the form of a research grant for carrying out the investigation and sincerely thanks the Syndicate for the same.

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ADSORPTION OF PERMANGANATE AND DYE-STUFFS BY PRECIPITATES

By

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Various theories have been advanced to explain the mechanism of adsorption. Bhatnagar and collaborators consider that during adsorption a physico-chemical complex between the adsorbent and the material adsorbed is formed and the properties of the substances in the adsorbed state are quite different from those of the original substances. Bhatnagar and Shrivastava (J. Phys. Chem., 1924, **28**, 730) observed that when sugar solutions are mixed with sols of arsenic and antimony sulphides, the actual rotation is less than that expected according to Beer's law. By simple combustion experiments, they showed that the elements constituting the sugar molecules were present in the coagula but their solutions in suitable solvent did not show any rotation. Bhatnagar, Shrivastava, Gupta and Prasad (J. Phys. Chem., 1925, **29**, 166) extended these observations to the adsorption of several sugars by other colloidal solutions and fine powders of insoluble substances and came to the same conclusions. Bhatnagar, Prasad and Bahl (J. Indian Chem. Soc. 1925, **2**, 11) showed that when soaps are adsorbed by colloidal particles and by finely divided precipitates, they lose their property of dissolving in water and lowering its surface tension although the constituents of soaps are present in the precipitates and the coagula.

In the present investigation, the authors have studied the adsorption of potassium permanganate and of certain dyestuffs by finely divided precipitates of insoluble substances with a view to collect further evidence in favour of the physico-chemical theory of adsorption.

EXPERIMENTAL

Merck's pure powders of zinc and aluminium oxides, lead chloride, barium carbonate and barium sulphate were used as adsorbents. Particles of uniform size were obtained by sieving the powders through two sieves containing 60 and 90 meshes to an inch. One gram of the powders was weighed out in glass stoppered bottles and 50 c.c. of the solution of the substance to be adsorbed were added to it. The bottles were then shaken for some time and were kept aside for 24 hours. The supernatent solution was then carefully decanted and its concentration was determined.

The concentration of the permanganate solution was determined by titrating it with a standard solution of oxalic acid. The concentration of the dye solutions after adsorption was found colorimetrically by comparing the tint of this solution with the original solution from which the adsorption had taken place. The dyes used for adsorption were hydrochlorides of methylene blue, malachite green, Bismark brown, Congo red and benzopurpurine.

The results obtained are given in the following tables in which

C_1 = concentration (grams per litre) of adsorbate before adsorption,

C_2 = concentration (grams per litre) of adsorbate after adsorption,

x = amount (in grams) of substance adsolved from 50 c.c. of solution $= C_1 - C_2/20$.

and m = mass (in grams) of adsorbent.

TABLE I

Adsorption of Potassium Permanganate by Zinc Oxide.

C_1	C_2	C_1-C_2	x/m
3.160	3.122	0.038	0.00190
1.053	1.024	0.029	0.00145
0.790	0.764	0.026	0.00130
0.652	0.627	0.025	0.00125
0.423	0.399	0.024	0.00120
0.395	0.372	0.023	0.00115

Table II

Adsorption of Potassium Permanganate by Aluminium Oxide.

C_1	C_2	C_1-C_2	x/m
3.160	3.049	0.111	0.00555
1.580	1.492	0.088	0.00440
1.053	0.980	0.073	0.00365
0.790	0.720	0.070	0.00350
0.526	0.461	0.065	0.00325
0.451	0.389	0.062	0.00310
0.395	0.344	0.051	0.00255

Table III

Adsorption of Methylene Blue by Barium Sulphate.

C_1	C_2	C_1-C_2	x/m
0.800	0.720	0.080	0,00400
0.500	0.430	0.070	0.00350
0.400	0.329	0.071	0.00355
0.250	0.197	0.053	0.00265
0.100	0,060	0.040	0.00200
0.080	0.043	0.037	0.00185

Table IV

Adsorption of Methylene Blue by Lead Chloride.

C_1	C_2	C_1-C_2	x/m
0,800	0.680	0.120	0.00600
0.500	0.388	0.112	0.00560
0.400	0.298	0.102	0.00510
0.250	0.158	0.092	0.00460
0.100	0.038	0.062	0.00310
0,080	0.022	0.058	0.00290

TABLE V

Adsorption of Malachite Green by Barium Sulphate

C_1	C_2	C_1-C_2	x/m
0.800	0.655	0.145	0.00725
0.400	0.344	0.056	0.00280
0.200	0.170	0.030	0.00150
0.080	0.068	0.012	0.00060
0.050	0.040	0.010	0.00050
0.040	0.035	0.005	0.00025

TABLE VI

Adsorption of Malachite Green by Lead Chloride.

C_1	C_2	C_1-C_2	x/m
0.800	0.571	0.229	0.01145
0.500	0.400	0.100	0.00500
0.400	0.345	0.055	0.00275
0.200	0.171	0.029	0.00145
0.100	0.081	0.019	0.00095
0.080	0.071	0.009	0.00045
0.050	0.046	0.004	0.00020

TABLE VII

Adsorption of Bismark Brown by Barium Sulphate.

C_1	C_2	C_1-C_2	x/m
1.000	0.208	0.792	0.03960
0.500	0.131	0.369	0.01845
0.250	0.068	0.182	0.00910

TABLE VIII

Adsorption of Bismark Brown by Barium Carbonate.

C_1	C_2	C_1-C_2	x/m
1.000	0.154	0.846	0.04230
0.500	0.095	0.405	0.02025
0.250	0.048	0.202	0.01010
0.100	0.025	0.075	0.00375

TABLE IX

Adsorption of Congo Red by Barium Carbonate.

C_1	C_2	C_1-C_2	x/m
0.800	0.435	0.365	0.01825
0.500	0.143	0.357	0.01785
0.400	0.080	0.320	0.01600
0.250	0.028	0.222	0.01110
0.200	0.010	0.190	0.00950

TABLE X

Adsorption of Benzopurpurine by Barium Carbonate.

C_1	C_2	C_1-C_2	x/m
0.800	0.307	0.493	0.02465
0.500	0.179	0.321	0.01605
0.400	0.149	0.251	0.01255
0.200	0.000	0.200	0.01000

DISCUSSION OF RESULTS

The precipitates obtained after the adsorption of potassium permanganate were coloured pink and this colour could not be removed by washing them with water, alcohol and acetone. This shows that the adsorbed potassium permanganate is rigidly fixed to the adsorbents and has lost its property of dissolving in water. On making qualitative tests, the presence of both manganese and potassium was indicated in the precipitates. A few observations on the H-ion concentration determination indicated that the adsorption of potassium permanganate is probably ionic and that the permanganate ions are adsorbed to a greater extent than the potassium ions.

The precipitates obtained after the adsorption of dyes were coloured with the colour of the dye. The colloidal dyes-benzopurpurine, Congo-red and Bismark brown—could not be removed from the adsorbed state by shaking the powders after adsorption with water, alcohol and acetone. But the crystalloidal dyes—methylene blue and malachite green-could be partly extracted by water and acetic acid. Each washing removes a part of the adsorbed dye until a limit is reached when no more of the dyes could be removed. The total quantities extracted in this manner depends upon the solvent used. The process of extraction of the dye from the adsorbed state can be explained if it is assumed that dye ions are situated in the mobile layer of the adsorbed material round the adsorbent and they are replaced to a certain extent, depending upon their chemical and electrical affinity with the ions primarily adsorbed, by H-ions furnished by the acetic acid.

Incidentally, the results in Tables I-X show that the Freundlich's adsorption equation is obeyed as on plotting log C_s against log x/m, straight lines are obtained in all cases.

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PREPARATION AND PROPERTIES OF TRANSPARENT INORGANIC GELS

By

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Amongst the inorganic gels the silicic acid gel has been most extensively studied. It was first prepared by Berzelius (Ann. Phys., 1833, 38, 312) and later by Graham, Fleming (Zeit. Physik, 1902, 44, 427), Holmes (J. Phys. Chem., 1918, 22, 510) and Bhatnagar and Mathur (Koll. Zeit., 1922, 30, 368), in either opaque or translucent state. Prasad and Hattiangadi (J. Indian Chem. Soc., 1929, 6, 653) have, however, shown that transparent gels of silicic acid can be obtained if the H-ion concentration of the gel-forming mixtures is suitably altered.

During the last few years several gels of inorganic substances have been prepared in an opaque or translucent condition (cf. Prakash, Journal Allahabad University Studies, vol. VIII, 1932). An attempt was, therefore, made by the authors to prepare some of these gels in a transparent condition by suitably selecting the constituents of the gel-forming mixtures and adjusting their H-ion concentrations. One of them (thorium phosphate) has been prepared by Parmar, Mehta and Prasad (Proc. Ind. Acad. Sci., 1936, 3, 107) in a transparent condition by using phosphoric acid instead of potassium phosphate as one of the constituents of the gel-forming mixture. Transparent gels of ceric phosphate described in this paper have been prepared for the first time.

Mehta, Parmar and Prasad (J. Indian Chem. Soc., 1936, 13, 128) have shown that transparent gels of thorium phosphate can also be obtained if a solution of thorium phosphate in concentrated hydrochloric acid is suitably diluted. Some gels prepared by this method have also been studied in this investigation.

It is well known that the time of setting of a gel depends upon the conditions of its preparation, namely, upon the concentration of the constituents of the gel-forming mixture, the H-ion concentration, the presence of the extra amounts of electrolytes, and non-electrolytes, the temperature, etc.

The effect of the concentration of the constituents of the gel-forming mixture on the time of setting has been studied by various workers. Fleming (Zeit. physikal Chem., 1902, 4, 427) found that the time of setting of the silicic acid gels increases with increasing concentration of the silicate solution. Prakash and Dhar (J. Indian Chem. Soc., 1929, 6, 587) who prepared a large number of inorganic gels found that, in general, the time of setting of gels increases with decreasing concentration of the salts containing the acidic ion of the gelling substance. Prasad and Hattiangadi (J. Indian Chem. Soc., 1929, 6, 653) showed that the addition of solutions of neutral ammonium acetate of increasing concentrations to the same solution of sodium silicate decreases the time of setting of the gels; high concentrations give flocculent precipitates instead of gels. However, if acidic ammonium acetate is used, the time of setting at first decreases, reaches a minimum, and then increases once again. Hurd and Miller (J. Phys. Chem., 1934, 38, 663) also found that the time of setting of silicic acid gels formed from sodium silicate and acetic acid increases on increasing the amount of acetic acid and sodium silicate. Parmar, Mehta and Prasad (loc. cit.) observed in the case of the thorium phosphate gels that the time of setting decreases with an increase in the concentration of phosphoric acid while it increases with an increase in the amount of thorium nitrate in the gel-forming mixtures.

Prakash and Dhar (J. Indian Chem. Soc., 1929, 6, 391) found that there is a considerable decrease in the H-ion concentration of the gel-forming mixture during gelation; in some cases the decrease amounts to 50 per cent of the original value. Prasad and Hattiangadi (J. Indian Chem. Soc., 1929, 6, 893) found that the pH of the silicic acid gel-forming mixture changes with a change in the concentration of the silica and the acid; with alkaline gel-forming mixture it increases during and after gelation but no perceptible change is noticed in the acidic mixtures. Hurd and Griffeth (J. Phys. Chem., 1935, 39, 1155) also did not notice any change in the pH value during and for sometime after the setting of mixtures of pH range 4·62-4·92. Hurd and Miller (J. Phys. Chem., 1934, 38, 663), however, found that the time of setting of gels obtained from sodium silicate and acetic acid within the pH range 4·14-6·00, varies linearly with the H-ion concentration. They further found that the addition of chloride, sulphate, and nitrate does not cause any considerable change in the pH.

It has been observed by several workers that some of the properties of gels alter when their conditions of formation are varied. The changes in the refractive index of the gel-forming system have been particularly studied. Frei (Koll. Zeit., 1910, 6, 192) and Walpole (*ibid.*, 1913, 13, 241) measured the refractive index of hydrosols of gelatin over a limited range of concentration and both of them concluded that the refractive index is a linear function of concentration. Hatscheck (Trans. Farad. Soc., 1920 16, 35) found that if the refractive index of organic gels is plotted against the temperature over a range containing the setting point, no discontinuity occurs at the gelatin point. Mardles (Trans. Farad. Soc., 1922, 78, 365), however, found some indication of a change in refractive index during the reversible sol to gel transformation of organosols. Hanstock (Trans. Farad. Soc., 1934, 30, 566) also observed an increase in the refractive index of gels of sodium benzoate on the passage from sol to gel state.

In the present investigation the time of setting of various transparent gels containing different amounts of the two constituents of the gel-forming mixtures and their H-ion concentration have been measured and the refractive indices of these mixtures have also been determined during the process of setting.

Experimental

(a) PREPARATION OF GELS.

In order to prepare gels a known volume of the solution of one of the constituents of the gel-forming mixture was taken in a test tube. In another test tube was taken a known volume of the solution of the other constituent together with some volume of distilled water and, in some case, some quantity of a solution of an acid, so as to make up the total volume of the mixture to 10 c. c. when the two solutions were mixed. The mixing was done as follows :—

The contents of one test tube were poured in the other and the mixture was shaken for about 15 seconds. It was then poured into the former test-tube which was gently inverted twice and then left over for the gel-forming mixtures to set. This method of mixing was followed throughout the investigation.

(b) DETERMINATION OF THE TIME OF SETTING

The time of setting was determined by Fleming's method. The accuracy of these measurements was increased by repeating the observations several times and each time disturbing the mixture as few times as possible during setting. This enables one to determine the time of setting fairly accurately. The time of setting in each case was determined at constant temperature. For this purpose the solutions of the constituents of the gel-forming mixtures were kept in two different test tubes for half an hour in the thermostat maintained at 30° before they were mixed.

(c) MEASUREMENT OF H-ION CONCENTRATION.

The quinhydrone method of measuring pH was employed as all the gel-forming mixtures are acidic. The apparatus was standardised by means of buffer solutions, M/20 potassium hydrogen phthalate (pH = 3.97) and M/20 borax (pH = 9.15).

For measuring the e.m.f. of the gel-forming mixtures the two constituents were separately mixed with solid quinhydrone and left overnight. They were then mixed and the e.m.f. was measured at 30° directly on the Cambridge Portable potentiometer. The pH was calculated from the relation :—

$$\mathrm{pH} = \frac{0.4535 - \mathrm{E\ (obs.)}}{0.06}$$

(d) DETERMINATION OF THE REFRACTIVE INDEX.

The refractive indices of the gel-forming mixtures were determined by means of Pulfrich Refractometer at 30°. The apparatus was standardised before use.

(A) THORIUM ARSENATE GELS.

These gels were first prepared by Prakash and Dhar (J. Indian Chem. Soc., 1929, 6, 587) in an opaque or translucent state by mixing 0.2 c.c.—0.4 c.c. of a 18 per cent solution of potassium arsenate made to 1.0 c.c. by the addition of water, with 5.0 c.c. of a solution of thorium nitrate (12.035 g. in 250 c.c.). They found that these gels are very stable and do not undergo syneresis.

It was found that transparent gels of thorium arsenate can be prepared if a solution of arsenic acid instead of that of potassium arsenate is used. On mixing the constituents of the gel-forming mixture a clear solution is obtained which becomes slightly turbid on standing and then sets to a firm transparent gel. The gels obtained are either transparent or slightly turbid. The turbidity, however, increases after setting, and after some time all gels become translucent. They are stable, thixotropic and do not synerise.

Thorium nitrate solution containing 60 g. a litre (thoria content, 2.8 per cent) and arsenic acid solution, containing 100 g. a litre (As_2O_3 content, 8.51 per cent) were used. The time of setting of the gel-forming mixtures containing varying amount of arsenic acid and thorium nitrate and their pH and refractive indices are given in tables I, II and III.

TABLE I

(a) Thorium nitrate—5.0 c.c.		(b) Arsenic acid—0.60 c.c.	
Arsenic acid	Time of set	Thorium nitrate	Time of set
0.90 c.c.	1'	2.0 c.c.	...
0.80 „	2'	3.0 „	62'
0.70 „	5'	3.4 „	34'
0.60 „	10'	3.6 „	28'
0.54 „	20'	4.0 „	20'
0.52 „	27'	4.4 „	15'
0.50 „	38'	5.0 „	10'
0.40 „	12 hrs.	5.4 „	9'
0.30 „	does not set	6.0 „	8'
		6.6 „	9'
		7.0 „	10'
		8.0 „	15'
		8.6 „	20'
		9.0 „	28'

TABLE II

(a) Thorium nitrate—5.0 c. c.			(b) Arsenic acid—0.6 c.c.		
Arsenic acid	Time of set	pH	Thorium nitrate	Time of set	pH
0.7 c. c.	5'	1.32	3.0 c. c.	62'	1.34
0.6 „	10'	1.37	5.0 „	10'	1.32
0.5 „	38'	1.44	7.0 „	10'	1.35
0.4 „	12 hrs.	1.52	9.0 „	28'	1.35

TABLE III

(*a*) Thorium nitrate—5.0 c. c.		(*b*) Arsenic acid—0.6 c.c.	
Arsenic acid	R. Index.	Thorium nitrate.	R. Index.
0.9 c.c.	1.33476	3.0 c.c.	1.33318
0.7 „	1.33456	4.0 „	1.33384
0.5 „	1.33444	5.0 „	1.33448
0.3 „	1.33436	6.0 „	1.33516
		7.0 „	1.33584
		8.0 „	1.33648
		9.0 „	1.33716

GELATION BY DILUTION

For this purpose thorium arsenate was prepared by adding excess of potassium arsenate to a solution of thorium nitrate and washing the gelatinous precipitate free from impurities by hot distilled water and drying it in an air oven at 110°. A saturated solution of the precipitate was made in hydrochloric acid (30 g. of the substance in 250 c. c. of 2·926N acid ; thoria content 3·144 per cent, and a known volume of it was diluted to different extent. The time of set obtained when different volumes of this solution are differently diluted is given in table IV in which

X = c.c. of thorium arsenate solution.

and Y = c.c. of water.

TABLE IV

Y	X=1.0	X=1.5	X=2.0	X=2.5
	Time of set	Time of set	Time of set	Time of set
5	...	...	...	...
10	3'	...	...	...
15	15'	2'	2'	...
20	does not set	9'	3'	2'
25		30'	6'	3'
30		does not set	20'	4'
35			50'	12'
40			does not set	28'
45				does not set

(B) THORIUM PHOSPHATE GELS.

These gels were prepared in the same manner as by Parmar, Mehta and Prasad (loc. cit.) from the same solution of thorium nitrate as used in (A) and 2N phosphoric acid.

The pH and the refractive indices of the various gel-forming mixtures are given in tables V and VI.

TABLE V

(*a*) Thorium nitrate – 5.0 c. c.			(*b*) Phosphoric acid – 0·9 c. c.		
Phosphoric acid	Time of set	pH	Thorium nitrate	Time of set	pH
0.9 c. c.	2'	1.12	5.0 c. c.	2'	1.12
0-8 c. c.	18'	1.17	6.0 c. c.	23'	1.12
0.7 c. c.	72'	1.22	7.0 c. c.	49'	1.12
0.6 c. c.	180'	1.29	8.0 c. c.	105'	1.12
0.5 c. c.	12 hrs.	1.36			

TABLE VI

(a) Thorium nitrate – 5.0 c. c.		(b) Phosphoric acid – 0.8 c. c.	
Phosphoric acid	R. Index	Thorium nitrate	R. Index
0.9 c. c.	1.33460	5.0 c. c.	1.33456
0.8 c. c.	1.33456	6.0 c. c.	1.33532
0.7 c. c.	1.33456	7.0 c. c.	1.33652
0.5 c. c.	1.33452	8.0 c. c.	1.33732

GELATION BY DILUTION.

For this purpose thorium phosphate was prepared in the same manner as thorium arsenate using potassium phosphate instead of potassium arsenate. A saturated solution of thorium phosphate was made in hydrochloric acid (20 g. of the substance in 250 c. c. of 2.96N acid; thoria content 1.292 per cent) and the time of set obtained when different volumes of this solution are differently diluted is given in table VII.

TABLE VII

Y	X=0.5	X=1.0	X=1.5	X=2.0	X=2.5
	Time of set	Time of set	Time of set	Time of set	Time of set
5	5′	2′	1′	1′	1′
10	12′	6′	3′	2′	1′
15	40′	10′	5′	3′	3′
20	does not set	18′	9′	6′	5′
25		28′	15′	10′	7′
30		60′	28′	16′	11′
35		does not set	45′	26″	17′
40			does not set	40′	25′
45				60′	35′
50				does not set	50′

(C) THORIUM MOLYBDATE GELS

These gels were first prepared by Prakash and Dhar (J. Indian Chem. Soc., 1929, 6, 587 ; *ibid*, 1930, 7, 367) in a transparent state by adding 0.3 c. c. – 0.8 c. c. of 10 per cent solution of potassium molybdate made to 1.0 c. c. by the addition of water, to 5.0 c. c. of a solution of thorium nitrate (12.035 g. in 250 c. c.). They found that the gels are very stable and do not synerise.

It was found that the transparency of the gel is considerably increased if some quantities of hydrochloric acid solution are added to the above mentioned gel-forming mixture. On mixing the constituents of the gel-forming mixture a gelatinous precipitate is obtained which dissolves on shaking and a clear solution is obtained which sets to a firm transparent gel. The gels obtained are clear and transparent, stable, highly thixotropic and do not synerise.

The same solution of thorium nitrate as in (A), 10 per cent solution of potassium molybdate and 2N hydrochloric acid were used.

The time of set of the gel-forming mixtures containing varying amount of hydrochloric acid, potassium molybdate and thorium nitrate and their pH and refractive indices are given in the following tables :

TABLE VIII

Thorium nitrate – 5.0 c. c.

Potassium molybdate – 1.0 c. c.

Hydrochloric acid	Time of set	Remarks
0.00 c. c.	36'	Opaque gel.
0.20 c. c.	2'	Translucent gel.
0.40 c. c.	4'	"
0.60 c. c.	6'	"
0.80 c. c.	5'	Transparent gel with slight turbidity.
1.00 c. c.	4'	"
1.20 c. c.	3'	"
1.40 c. c.	2'	Clear, transparent gel.
1.60 c. c.	3'	"
1.80 c. c.	8'	"
1.90 c. c.	13'	"
1.96 c. c.	18'	"
2.00 c. c.	32'	"

TABLE IX

Thorium nitrate— 5.0 c. c.

Potassium molybdate	Hydrochloric acid			
	0.2 c. c. Time of set	0.6 c. c. Time of set	1.4 c. c. Time of set	2.0 c. c. Time of set
1.00 c. c.	2′	6′	2′	32′
0.90 „	3′	...	...	18′
0.80 „	5′	7′	3′	10′
0.70 „	9′	...	...	5′
0.60 „	16′	10′	4′	6′
0.54 „	24′	...	...	...
0.50 „	40′	13′	5′	8′
0.40 „	12 hrs.	22′	7′	16′
0.34 „	does not set	44′	...	...
0.30 „		12 hrs.	20′	32′
0.26 „		does not set	48′	60′
0.20 „			does not set	does not set

TABLE X

Potassium molybdate — 1.0 c. c.

Thorium nitrate	Hydrochloric acid	
	0.6 c. c. Time of set	2.0 c. c. Time of set
3.0 c. c.	ppt.	ppt.
4.0 „	„	„
5.0 „	6′	32′
6.0 „	7′	22′
7.0 „	8′	13′
8.0 „	9′	...

TABLE XI

(a) Thorium nitrate 5.0 c. c. HCl 0.6 c. c.			(b) Potassium molybdate 1.0 c. c. HCl 2.0 c. c.			(c) Thorium nitrate 5.0 c. c. Potassium molybdate 1.0 c. c.		
Potassium molybdate	Time of set	pH	Thorium nitrate	Time of set	pH	HCl	Time of set	pH
1.0 c. c.	6′	1.69	5.0 c. c.	32′	0.91	0.0 c. c.	36′	2.96
0.6 „	10′	1.36	6.0 „	22′	0.91	0.2 „	2′	2.46
0.3 „	does not set	1.36	7.0 „	13′	0.91	0.6 „	6′	1.69
						1.4 „	2′	1.06
						2.0 „	32′	0.91

Table XI

(a) Thorium nitrate 5.0 c. c. HCl 1.4 „		(b) Potassium molybdate 1.4 c. c. HCl 2.0 „		(c) Thorium nitrate 5.0 c. c. Potassium molybdate 1.0 „	
Potassium molybdate	R. Index.	Thorium nitrate	R. Index	HCl	R. Index.
1.0 c. c.	1.33732	5.0 c. c.	1.33836	0.2 c. c.	Slit not clear.
0.8 „	1.33716	6.0 „	1.33892	0.6 „	1.33572
0.6 „	1.33700	7.0 „	1.33965	1.0 „	1.33669
0.4 „	1.33684			1.4 „	1.33732
0.2 „	1.33668			1.8 „	1.33792
				2.8 „	1.33836

(D) STANNIC PHOSPHATE GELS

These gels were first prepared by Prakash and Dhar (J. Indian Chem. Soc., 1929, 6, 587; 1930, 7, 367) by mixing 1.0 c.c. – 3.0 c.c. of a 22 per cent solution of potassium phosphate to 3.0 c.c. of M/1.099 solution of stannic chloride and making up the volume to 6.0 c.c. These gels are stable, show no syneresis and are translucent but become opaque on standing.

The transparency of the gel was found to increase considerably if a solution of phosphoric acid instead of that of potassium phosphate is used. On mixing the constituents of the gel-forming mixture a clear solution is obtained which becomes slightly turbid on standing and then sets to a firm transparent gel. The gels obtained are transparent with slight turbidity. On keeping, however, they become translucent or opaque. They are stable and do not synerise.

175.27 g. of stannic chloride (Merck's commercial) were dissolved in distilled water, to which 2.0 c.c. of concentrated nitric acid was added. The solution was heated to boiling for some time and after cooling it was made up to one litre. The stannic oxide content of the solution was found to be 7.16 per cent. 2N phosphoric acid was used.

The time of set of the gel-forming mixtures containing varying amounts of phosphoric acid and stannic chloride and their pH and refractive indices are given in the following tables:

TABLE XIII

(*a*) Stannic chloride – 3.0 c.c.		(*b*) Phosphoric acid – 1.0 c.c.	
Phosphoric acid	Time of set	Stannic chloride	Time of set
1.2 c.c.	2'	2.0 c.c.	1,
1.0 ,,	4'	3.0 ,,	4'
0.8 ,,	9'	4.0 ,,	22'
0.7 ,,	14'	5.0 ,,	85'
0.6 ,,	26'	6.0 ,,	4 hrs.
0.5 ,,	60'	7.0 ,,	12 hrs.
0.4 ,,	185'		
0.3 ,,	12 hrs.		

TABLE XIV

(a) Stannic chloride—3.0 c.c.			(b) Phosphoric acid—1.0 c.c.		
Phosphoric acid.	Time of set	pH	Stannic chloride	Time of set	pH
0.8 c.c.	9'	0.57	4.0 c.c.	22'	0.49
0.6 „	26'	0.59	6.0 „	4 hrs.	0.36
0.4 „	185'	0.61			
0.3 „	12 hrs.	0.62			

TABLE XV

(a) Stannic chloride—3.0 c.c.		(b) Phosphoric acid—1.0 c.c	
Phosphoric acid	R. Index	Stannic chloride	R. Index.
1.0 c.c.	1.33974	3.0 c.c.	1.33974
0.8 „	1.33965	4.0 „	1.34237
0.6 „	1.33953	5.0 „	1.34480
0.4 „	1.33941	6.0 „	1.34723
		7.0 „	1.34970

(E) STANNIC ARSENATE GELS

These gels were first prepared by Prakash and Dhar (J. Indian Chem. Soc., 1929, 6, 587 ; 1930, 7, 367) by mixing 3.0 c. c. of M/1.099 solution of stannic chloride with about 2.0 c. c. of 18 per cent solution of potassium arsenate and making up the volume to 6.0 c. c. They are translucent at the time of formation but become opaque on keeping. They are stable and do not synerise.

In the present investigation a solution of arsenic acid instead of that of potassium arsenate was used. On mixing the constituents of the gel-forming mixture, a clear solution is obtained which becomes slightly turbid on keeping and then sets to a firm transparent gel. The gels obtained are transparent and slightly turbid. On keeping, however, they become translucent or opaque They are stable and do not synerise.

The same solution of stannic chloride as in (D) and of arsenic acid as in (A) were used.

The time of set of the gel-forming mixtures containing different amounts of arsenic acid and stannic chloride and their pH and refractive indices are given in tables XVI, XVII and XVIII.

TABLE XVI

(a) Stannic Chloride—3.0 c.c.		(b) Arsenic Acid—1.0 c.c.	
Arsenic Acid	Time of set	Stannic Chloride	Time of set
1.2 c.c.	2'	2.0 c.c.	1'
1.0 „	4'	3.0 „	4'
0.8 „	10'	4.0 „	36'
0.7 „	16'	5.0 „	4 hrs.
0.6 „	32'	6.0 „	12 hrs.
0.5 „	68'		
0.4 „	4 hrs.		
0.3 „	12 hrs.		

TABLE XVII

(a) Stannic Chloride—3.0 c.c.			(b) Arsenic Acid—1.0 c.c.		
Arsenic Acid	Time of set	pH	Stannic Chloride	Time of set	pH
1.0 c.c.	4'	0.57	4.0 c.c.	36'	0.44
0.7 „	16'	0.59	6.0 „	4 hrs.	0.12
0.5 „	68'	0.61			

TABLE XVIII

(a) Stannic Chloride—3.0 c.c.		(b) Arsenic Acid—1.0 c.c.	
Arsenic Acid	R. Index	Stannic Chloride	R. Index
1.0 c.c.	1.34015	3.0 c.c.	1.34015
0.8 „	1.33990	4.0 „	1.34279
0.6 „	1.33961	5.0 „	1.34766
0.4 „	1.33941	6.0 „	1.34766

(F) MANGANESE ARSENATE GELS

These gels were first prepared by Deiss (Koll. Zeit., 1914, 14, 39 ; 1915, 15, 16 ; Zeit. anorg. Chem., 1921, 166, 228) by mixing suitable solutions of manganese chloride and potassium arsenate and were found to be very stable. However, after some time rose coloured crystals were found to separate out. Klemp and Gyulai (Koll. Zeit, 1914, 15, 202) obtained these gels by the successive addition of ammonium sulphate, acetic acid and excess of sodium arsenate to solutions of manganous salts, in the opalescent state. The crystals separated out in these gels as well, on keeping. Weiser and Bloxson (J. Phys. Chem., 1924, 28, 26) and Kraemer (Colloid. Symp. Mono. Wisconsin., 1923, 1, 62) prepared them by adding manganese sulphate to the solution of potassium arsenate (KH_2AsO_4) and found that a slight warming hastens the gel formation. They, however, did not measure the time of setting.

Attempts were made to prepare manganese arsenate gels by using solutions of manganese salts and arsenic acid of various concentrations but in no case a gel was formed. Consequently these gels were prepared by the same method as followed by Weiser and co-workers. On mixing the constituents of the gel-forming mixture a clear solution is obtained which sets to a clear transparent gel on standing. The gels obtained are perfectly transparent throughout the entire process of gelation. They are stable and do not synerise. No separation of the crystals was observed even when the gels are kept for several months.

Manganese chloride solution (100 g. in a litr and potassium arsenate solution (180 g. in a litre) were used.

The time of set of the gel-forming mixtures containing varying amount of potassium arsenate and manganese chloride and their pH and refractive indices are given in the following tables:—

TABLE XIX

(*a*) Manganese chloride—4.0 c.c.		(*b*) Potassium arsenate—1.0 c.c.	
Potassium arsenate	Time of set	Manganese chloride	Time of set
1.2 c.c.	1'	3.0 c.c.	2'
1.1 „	1'	4.0 „	2'
1.0 „	2'	6.0 „	3'
0.9 „	3'	8.0 „	does not set
0.8 „	5'		
0.7 „	does not set		

TABLE XX

(*a*) Manganese chloride—4.0 c c.			(*b*) Potassium arsenate—1.0 c.c.		
Potassium arsenate.	Time of set	pH	Manganese chloride	Time of set	pH
1.0 c. c.	2′	3.09	2.0 c. c.	2′	3.26
0.9 „	3′	3.12	4.0 „	2′	3.69
0.8 „	5′	3.16	6.0 „	3′	3.06
0.7 „	does not set	3.19			

TABLE XXI

(*a*) Manganese chloride—4.0 c. c.		(*b*) Potassium arsenate—1.0 c. c.	
Potassium arsenate	R. Index	Manganese chloride	R. Index
1.1 c. c.	1.33828	2.0 c. c.	1.33548
0.9 „	1.33796	4.0 „	1.33812
0.7 „	1.33764	6.0 „	1.34072

(G) ZINC ARSENATE GELS

These gels were first prepared by Klemp and Gyulai (Koll. Zeit., 1918, 22, 57) by adding solutions of potassium dihydrogen arsenate to a solution of zinc sulphate. They also obtained gels when solutions of disodium and trisodium arsenates neutralised by hydrochloric or acetic acid were used in place of potassium dihydrogen arsenate. On keeping these gels for two or three months, crystals of zinc arsenate separate out. Weiser and Bloxson (J. Phys. Chem., 1924, 28, 26) prepared these gels by using solutions of zinc sulphate and dipotassium hydrogen arsenate. The gels obtained are less stable and even the dilute ones become cloudy in a few days owing to the formation of crystals. They, however, did not measure the time of setting of these gels.

Zinc arsenate gels were prepared by using solutions of zinc sulphate and potassium arsenate. On mixing the constitutents of the gel-forming mixture a clear solution is obtained which sets to a clear transparent gel on standing. The gels obtained are perfectly transparent throughout the entire process of gelation. They are stable and do not synerise. They become cloudy but no separation of the crystals was observed when they are kept for two months.

Zinc sulphate solution (100 g. a litre) and the same solution of potassium arsenate as used in (F) were used.

The time of set of the gel-forming mixtures containing varying amount of potassium arsenate and their pH and refractive indices are given in the following tables.

TABLE XXII

Zinc sulphate–4.0 c. c.

Potassium arsenate	Time of set
0.35 c. c.	2′
0.30 „	5′

TABLE XXIII

Zinc sulphate–4.0 c. c.

Potassium arsenate	Time of set	pH	R. Index.
0.35 c. c.	2′	3.14	1.33564
0.30 „	5′	3.17	1.33544

(H) CERIC PHOSPHATE GELS.

These gels were prepared for the first time by mixing solution of potassium phosphate (K_2HPO_4) with that of cerium nitrate. No gels were obtained when phosphoric acid and potassium phosphate (KH_2PO_4) were used. On mixing the constituents of the two solutions a white precipitate is obtained which dissolves more or less on shaking and this solution on keeping sets to a transparent gel. The gels are transparent and slightly turbid. They are highly thixotropic and do not synerise.

Cerium nitrate solution (100 g. a litre) and potassium phosphate solution (200 g. a litre) were used.

The time of set of the gel-forming mixtures containing varying amounts of potassium phosphate and cerium nitrate and their pH are given in the following tables :

TABLE XXIV

(*a*) Cerium nitrate – 5.0 c. c.		(*b*) Potassium phosphate – 0.8 c. c.	
Potassium phosphate	Time of set	Cerium nitrate	Time of set
1.1 c. c.	28'	4.0 c. c.	36'
1.0 „	32'	5.0 „	44'
0.8 „	44'	6.0 „	64'
0.7 „	80'	7.0 „	does not set
0.6 „	does not set		

TABLE XXV

(*a*) Cerium nitrate – 5.0 c. c.			(*b*) Potassium phosphate – 0.8 c. c.		
Potassium phosphate	Time of set	pH	Cerium nitrate	Time of set.	pH
1.0 c. c.	32'	1.56	4.0 c. c.	36'	1.69
0.8 „	44'	1.62	5.0 „	44'	1.62
0.7 „	80'	1.69	6.0 „	64'	1.52

The refractive indices of these gels could not be determined because of the blurring of the slit.

DISCUSSION

The above tables give the limits of the amounts of the constituents of the gel-forming mixtures which give rise to transparent gels. If these limits, either of the salt which contains the cation of the gelling substance, designated as salt I hereafter, or of the salt which contains the anion of the gelling substance, designated as salt II, are exceeded, then either a precipitate is obtained or the gel does not set. If the amount of the salt I is more or less than the limited amount, the concentration of the peptising ions in the mixture is either too low or too great and either a curd or a viscous mass is formed. On the other hand if the quantity of the salt II is more or less than the limited amount, the quantity of the gelling substance in the mixture is either very large or very small. In the first case the amount of the metal ions which peptise the precipitate of the gelling substance is small and hence the precipitate does not go over to the colloidal state but settles down as a curd. In the latter case, however, the amount of the peptising ions is large and that of the gelling substance small and hence sufficient number of highly dispersed micelles is not available to enmesh the whole of the liquid and a viscous mass is obtained.

The effect on the time of setting of the addition of increasing quantities of salt I and salt II is shown in the following table:

TABLE XXVI

Name of the gel	Salt I	Salt II
Thorium arsenate	decreases at first, reaches a minimum, then increases.	decreases
Thorium molybdate	increases; with 2.0 c.c. of acid decreases.	decreases; with 2.0 c.c of acid decreases, reaches a minimum and then increases.
Manganese arsenate	increases	decreases
Zinc arsenate	—	decreases
Stannic phosphate	increases	decreases
Stannic arsenate	increases	decreases
Ceric phosphate	increases	decreases

The addition of increasing quantities of salt I to the same quantity of salt II increases the concentration of metal ions and hence the degree of dispersity of the same amount of the gelling substance and the density of charge on the colloid particles is increased. This decreases the rate of coagulation of the colloid particles of the gelling substance formed in the gel-forming mixtures and delays the time of setting of the gels. This behaviour has been observed in all gels excepting in gels of thorium arsenate and thorium molybdate.

The effect of the addition of increasing quantities of salt II is to decrease the time of setting of all the gel-forming mixtures. The decrease in the time of setting may be due to an increase in the amount of (i) the gelling substance and the consequent decrease in the amount of the peptising (metal) ions and (ii) the coagulating electrolyte. These circumstances result in giving rise to a large number of colloidal particles having a low density of charge and favour an increase in the rate of coagulation and the consequent decrease in the time of setting. A peculiarity has, however, been observed in the case of thorium molybdate gel-forming mixture containing 2.0 c.c. of the hydrochloric acid solution as in this case the time of setting first decreases, reaches a minimum and then increases.

The peculiar behaviour of thorium molybdate gels in the presence of different quantities of hydrochloric acid is shown in fig. 1. It will be seen from the figure that with an increase in the quantity of hydrochloric acid in the gel-forming mixture the time of setting first decreases, reaches a minimum, then increases and again decreases to a second minimum followed by a rapid rise. When a solution of potassium molybdate is added to thorium

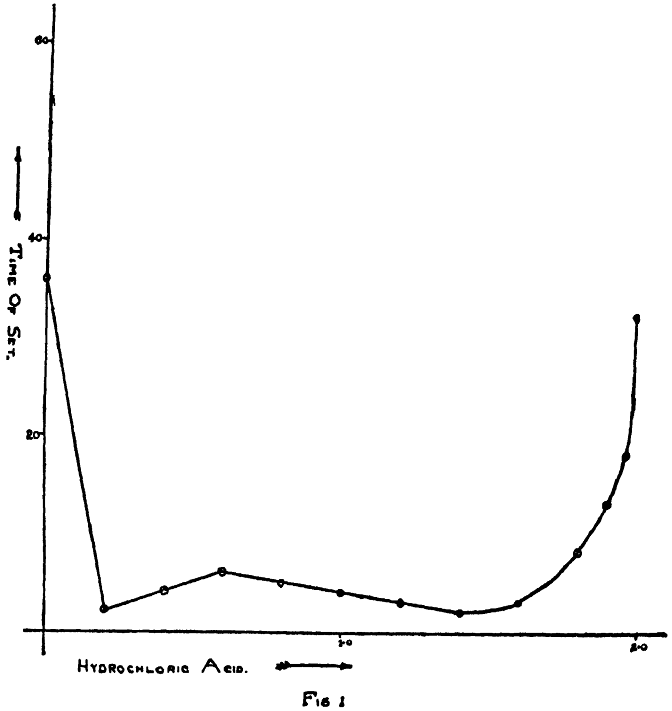

FIG 1

nitrate it is observed that a precipitate of thorium molybdate disappears or is peptised with great difficulty. This shows that the colloid particles of the gelling substance in mixtures containing no hydrochloric acid are fairly big. This view is supported by the fact that the gels obtained are opaque (cf. table VIII). When, however, acid is added to the mixture the precipitate of thorium molybdate is peptised readily and the gels obtained are translucent, that is, they contain particles carrying increased density of charge which causes an increase in the time of setting. The density of charge on the particles is, however, not very great. This may be due to the fact that when potassium molybdate is added to a small quantity of hydrochloric acid molybdic acid gets precipitated and dissolves on slight shaking. Vigorous shaking is required with solutions containing 0.6 c.c. of the acid in order to obtain a clear solution. The molybdic acid formed by the interaction of potassium molybdate and hydrochloric acid probably goes over to the colloidal condition in these mixtures and peptises the precipitated thorium molybdate and thus causes an increase in the time

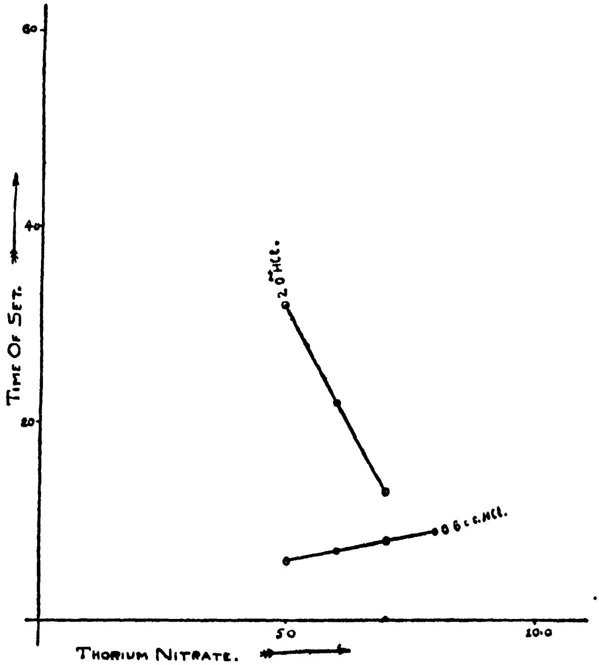

Fig. 3.

of setting. The addition of further quantities of hydrochloric acid from 0.6 c.c. to 1.4 c.c. causes a dissolution of colloidal molybdic acid to the crystalloidal state, thereby the peptising influence of the colloidal molybdic acid is removed and the gels set in a slightly shorter time than before. The addition of further quantities of the acid results in a great increase in the dispersity of the gelling particles, due to an increase in the density of charge in the presence of large amount of H-ions, and thereby the time of set is considerably increased. The gels formed under these conditions are quite transparent which shows that the gelling particles are present in a very finely subdivided state.

These considerations are supported by the effect of the addition of increasing amount of thorium nitrate to potassium molybdate containing different quantities of hydrochloric acid. It will be seen from fig. 3 that the addition of increasing amount of thorium nitrate to mixtures containing 0.6 c.c. of hydrochloric acid increases the time of setting of the gels and thereby shows that the

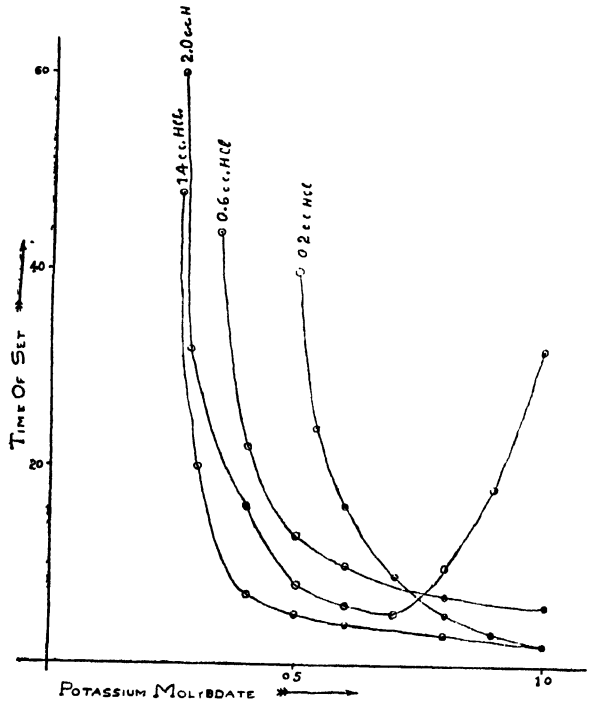

Fig. 2.

density of charge on the particles is not large and an increase of thorium ions in the mixture can cause a further increase in the degree of dispersity of the gelling particles and thereby delay the time of setting. But a similar effect in the case of a mixture containing 2.0 c.c. of hydrochloric acid shows a decrease in the time of setting because the gelling particles are already in a highly peptised condition and the addition of increasing quantities of thorium nitrate merely increases the concentration of the coagulating ion.

The effect of the increasing quantity of potassium molybdate in mixtures containing different amounts of hydrochloric acid is shown in fig. 2. It will be seen that the behaviour of the mixture containing 0.2, 0.6 and 1.4 c.c. of hydrochloric acid is a normal one, in that the time of setting uniformly decreases. But in mixtures containing 2.0 c.c. of hydrochloric acid the time of setting first decreases, reaches a minimum and then increases. It is probable that in these mixtures sufficient amount of molybdic acid is formed in the colloidal state and this may be effecting an increase in the setting time beyond the minimum point

It is difficult to explain at present the decrease in the time of setting of thorium arsenate gels when the amount of thorium nitrate in the gel-forming mixture is increased. The increase in the time of setting beyond the minimum is, no doubt, due to the peptising influence of thorium ions.

The results of pH measurements of all the gel-forming mixtures when the quantities of salt I and salt II are increased in the mixture are summarised in the following table.

TABLE XXVII

Gels	Effect on pH on increasing	
	Salt I	Salt II
Thorium arsenate	no change	decreases
Thorium phosphate	no change	decreases
Thorium molybdate	no change	no change; with increase in acid content decreases
Manganese arsenate	decreases	decreases
Zinc arsenate	—	decreases
Stannic phosphate	decreases	decreases
Stannic arsenate	decreases	decreases
Ceric phosphate	decreases	decreases

It will be seen that an increase in the quantity of salt I in thorium arsenate, thorium phosphate and thorium molybdate gel-forming mixtures produces no change in pH but in all the other cases the addition of salt I and salt II increases the H-ion concentration of the mixture. It will be seen that in all cases the quantity of salt I taken for the formation of gels is in excess of the salt II and, therefore, no change in the pH value of the gel-forming mixtures for the first three gels, on the addition of increasing quantities of thorium nitrate indicates that it does not hydrolyse appreciably under the conditions of the experiment while a good deal of hydrolysis takes place with other salts (salt I). The decrease in pH with increasing quantities of salt II is expected as acids have been used in all cases excepting in the preparation of manganese arsenate and zinc arsenate gels.

An important observation is that no change in pH takes place during the gelation of all the gels studied herein. This is in agreement with the observations of Hurd and co-workers (loc. cit.) and of Prasad and Hattiangadi (loc. cit.) who also observed no change in the pH of acidic silicic acid gel-forming mixtures during setting.

The refractive indices of all the gel-forming mixtures increase as the amount of the salt I and salt II in the mixture is increased. This is in agreement with the observations of previous workers.

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A STUDY OF THE DECOMPOSITION OF NAPHTHOL ETHERS BY HALOGEN ACIDS AND BY ALCOHOLIC CAUSTIC POTASH AND DETERMINATION OF THE VELOCITY CONSTANTS

By

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I. INTRODUCTORY :—

Compared with esters, aliphatic and aromatic ethers are more stable towards halogen acids. Prior to 1927 little work was done on this subject. In recent years, however, considerable work on this subject has been done. Towards alkalies, ethers are far more stable than esters. Ethers employed in these earlier investigations were mainly ethers of phenol and substituted phenols, but little work was done on ethers of naphthols and substituted naphthols.

In the present investigation the decomposition of ethers of naphthols and substituted naphthols in the presence of halogen acids with acetic acid as a solvent is studied as a time reaction. In a few cases formic acid, propionic acid and N-butyric acid are also employed as solvents. The decomposition of a few ethers in the presence of alcoholic potash is also studied. The influence of a variation of temperature and the presence of varying amounts of water on the reaction is also studied. The results are given in tables that follow:—

I. EXPERIMENTAL

Materials :—The ethers mentioned in Table I (except anisol and phenetol) and the corresponding naphthols (except ∝ naphthol and β naphthol) were prepared in the laboratory by methods given in literature and by other methods analogous to them. They were then very carefully purified.

Methods of estimation :—In the case of the ethers, both of ∝ naphthol and β naphthol the course of the decomposition is followed by estimating the naphthol, liberated in the decomposition, by titration with a standard solution of diazotised p-nitraniline in a neutral solution, containing a fair excess of sodium acetate. (Schwalbe, Ber., *38*, 3072, 1905). In the case of ethers of substituted naphthols, the undecomposed ether in the reaction mixture is estimated by neutralising the reaction mixture by concentrated 1:2) solution of caustic soda. It is then rendered alkaline by adding 3 c.c. more of the above solution. The solution is then extracted twice by 25 c.c. of pure sulphuric ether. The etherial extract which contains the undecomposed naphthol ether is transferred to a weighed flask, the solvent ether evaporated on a water bath, and the flask containing the residue is kept in a vacuum desiccator till its weight becomes constant. When the decomposition of the ether is brought about by alcoholic potash, the undecomposed ether (except in the case of anisol and phenetol) in the reaction mixture is extracted by sulphuric ether, as above, and thus estimated. Further the alkaline solution is also acidified and the liberated naphthol is extracted with sulphuric ether and estimated. This serves as a check on the previous estimation of the undecomposed ether.

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* Details of the above investigation will be found in the thesis submitted by the latter author for the M.Sc. degree of the Bombay University in 1936.

In the case of anisol and phenetol, the part remaining undecomposed under the influence of hydrobromic acid or alcoholic potash, is removed by extraction with sulphuric ether and the phenol liberated in the reaction is estimated by employing a standard solution of potassium bromide and potassium bromate.

Method of experimentation and calculation :—The decomposition of all the ethers is studied at the boiling point of water. The ethers are dissolved in pure acetic acid and the decomposing agent used is constant boiling hydrobromic acid. The reaction probably runs according to the following equation :—

$ROR' + HB_r = ROH + R'B_r$ where 'R' stands for naphthyl radical and 'R'' for the alkyl radical ; and since the molar concentration of HB_r is about 20 times the molar concentration of the ether, the reaction can be regarded as a unimolecular one, an assumption which is justified by the concordant values obtained for the velocity constants.

II. DETAILS OF EXPERIMENTAL RESULTS :—

Detailed results obtained in a few cases are given below to show how far the mean value of the constant differs from the individual values ; each experiment being done in duplicate.

(1) *2-methoxynaphthalene* 0·1000 grm.
Solvent: 6 c.c. glacial acetic acid.
Decomposing agent: 1·5 c.c. constant boiling HBr.
Temperature: boiling water bath.

Time in minutes	c.cs. of Standard diazo Solution	Constants
30	8.5	0.01367
30	8.3	0.01326
60	14.3	0.01439
60	14.1	0.01389
90	18.3	0.01429
90	18.1	0.01397
Mean value of the constant		0.01391

(2) *2-ethoxynaphthalene* 0·1088 grm.
Solvent: 6 c.c. glacial acetic acid.
Decomposing agent: 1·5 c.c. constant boiling HBr.
Temperature: boiling water bath.

Time of minutes	c.cs. of Standard diazo Solution	Constants
40	10.00	0.01256
40	9.80	0.01226
80	16.10	0.01266
80	16.00	0.01252
120	20.00	0.01304
120	19.70	0.01265
Mean value of the constant		0.01261

One c.c. of the standard diazo solution
= 0·0036 grm. of β naphthol.

(3) *1—Bromo 2-methoxy naphthalene* 0.1500 grm.

Solvent : 6 c. c. glacial acetic acid.
Decomposing agent : 1.5 c. c. constant boiling HBr.
Temperature : boiling water bath.

Time in minutes	Wt. of undecomposed ether	Constants
60	0.1180	0.004000
60	0.1190	0.003863
120	0.0926	0.004024
120	0.0932	0.003971
180	0.0758	0.004065
180	0.0760	0.004052
Mean value of the constant	...	0.003995

(4) *1—Bromo-2-ethoxy naphthalene* 0.1588 grm.

Solvent : 6 c. c. glacial acetic acid.
Decomposing agent : 1.5 c. c. constant boiling HBr.
Temperature : boiling water bath.

Time in minutes	Wt. of undecomposed ether	Constants
60	0.1322	0.003061
60	0.1330	0.002956
120	0.1102	0.003059
120	0.1106	0.003018
180	0.0916	0.003059
180	0.0922	0.003024
Mean value of the constant		0.003027

(5) *1-Chloro-2-methoxy naphthalene* = 0.1218 grm.

Solvent : 6 c. c. glacial acetic acid.
Decomposing agent : 1.5 c. c. constant boiling HBr.
Temperature : boiling water bath.

Time in minutes	Wt. of undecomposed ether	Constants
62	0.1024	0.002798
62	0.1008	0.003063
120	0.0840	0.003097
120	0.0844	0.003059
180	0.0702	0.003063
180	0.0692	0.003070
Mean value of the constant		0.003025

(6) *I-Chloro-2-ethoxy naphthalene* = 0.1306 grm.

Solvent : 6 c. c. glacial acetic acid.
Decomposing agent : 1.5 c. c, constant boiling HBr.
Temperature : boiling water bath.

Time in minutes	Wt. of undecomposed ether	Constants.
60	0.1156	0.002028
60	0.1162	0.001939
120	0.1026	0.002009
120	0.1034	0.001945
180	0.0916	0.001972
180	0.0916	0.001972
Mean value of the constant		0.001977

(7) *Anisol* 0.1139 grm.

Solvent : 10 c. c. glacial acetic acid.
Decomposing agent : 2.5 c.c. constant boiling hydrobromic acid.
Temperature : boiling water bath.

Time in minutes	0.1N sodium thiosulphate for back titration. c.cs.	0.24N bromate bromide solution added c.cs.	constants.
94	13.4	15.0	0.004708
94	13.3	15.0	0.004732
180	13.4	20.0	0.004401
180	13.00	20.0	0.004451
270	16.0	25.0	0.004409
270	15.7	25.0	0.004465
Mean value of the constant			0.004527

(8) *Phenetol* 0.1286 grm.

Solvent : 10 c.c. glacial acetic acid.
Decomposing agent : 2.5 c.c, constant boiling hydrobromic acid.
Temperature : boiling water bath.

Time in minutes	0.1N sodium thiosulphate for back titration c.cs.	0.24N bromate bromide solution added c.cs.	constants.
120	19.0	15.0	0.002609
120	18.9	15.0	0.002627
240	17.9	20.0	0.002695
240	19.0	20.0	0.002558
360	21.8	25.0	0.002573
360	18.9	24.0	0.002629
Mean value of the constant			0.002615

III—TABULAR SUMMARY OF THE RESULTS OBTAINED :—

In getting the results given in Table I, II, III, and IV, a boiling water bath is employed for carrying out the decompositions.

TABLE I.

Solvent : glacial acetic acid *Decomposing agent : constant boiling hydrobromic acid.*

Name of ether	Mean velocity constant.
2-methoxynaphthalene	0.01391
2-ethoxynaphthalene	0.01261
1-methyl-2-methoxynaphthalene	0.01010
1-methyl-2-ethoxynaphthalene	0.005832
6-bromo-2-methoxynaphthalene	0.006446
6-bromo-2-ethoxynaphthalene	0.004713
1-bromo-2-methoxynaphthalene	0.003995
1-bromo-2-ethoxynaphthalene	0.003027
1-chloro-2-methoxynaphthalene	0.003025
1-chloro-2-ethoxynaphthalene	0.001977
1-nitro-2-methoxynaphthalene	0.0004826
1-nitro-2-ethoxynaphthalene	0.0002991
1-6-dibromo-2-methoxynaphthalene	0.002028
1-6-dibromo-2-ethoxynaphthalene	0.001356
1-chloro-6-bromo-2-methoxynaphthalene	0.001980
1-chloro-6-bromo-2-ethoxynaphthalene	0.001412
1-methoxynaphthalene	0 007385
1-ethoxynaphthalene	0.005778
4-bromo-1-ethoxynaphthalene	0.002542
4-nitro-1-methoxynaphthalene	0.0002529
4-nitro-1-ethoxynaphthalene	0.0001840
2-nitro-1-methoxynaphthalene	0.002880
anisol	0.004527
phenetol	0.002615

TABLE II.

Influence of water on the decomposition of 2-methoxy-naphthalene. Decomposing agent, 1.5 c.c. of constant boiling hydromic acid.

Name of the ether	Solvent.	Mean velocity constant.
2-Methoxynaphthalene	6. c.cs of acetic acid containing 0.298 grm. of water.	0.01180
do.	6. c.cs of acetic acid containing 0.577 grm. of water.	0.01053
do.	6. c.cs of acetic acid containing 1.155 grms. of water.	0.008677
do.	6 c.cs of acetic acid containing 2.311 grms. of water.	0.006319

TABLE III

Decomposition of 2-Methoxynaphthalene. 2-Ethoxynaphthalene, 1-Methoxynaphthalene and 1-Ethoxynaphthalene with Hydrochloric, Hydrobromic and Hydriodic Acids as the Decomposing Agents under Comparable Conditions

Name of the ether	Solvent	Decomposing agent	Mean value of the velocity constant
2-Methoxynaphthalene	5.5 c.cs. of glacial acetic acid	2 c.cs. of constant boiling HCl	0.005834
2-Ethoxynaphthalene	do	do	0.005128
1-Methoxynaphthalene	do	do	0.002226
1-Ethoxynaphthalene	do	do	0.002046

TABLE III—*(concld.)*

Name of the ether	Solvent	Decomposing agent	Mean value of the velocity constant
2-Methoxynaphthalene	6 c.cs. of acetic acid containing 0.5771 grm. of water	1.5 c.cs. of constant boiling HBr.	0.01053
2-Ethoxynaphthalene	do	do	0.009948
1-Methoxynaphthalene	do	do	0.005166
1-Ethoxynaphthalene	do	do	0.004575
2-Methoxynaphthalene	5.8 c.cs. of acetic acid containing 0.4957 grm. of water	1.7 c.cs. of constant boiling HI	0.02127
2-Ethoxynaphthalene	do	do	0.01602
1-Methoxynaphthalene	do	do	0.01175
1-Ethoxynaphthalene	do	do	0.007167
2-Methoxynaphthalene	5.8 c.cs. of glacial acetic acid	1.7 c.cs. of constant boiling HI	0.03592
2-Ethoxynaphthalene	do	do	0.01784
1-Methoxynaphthalene	do	do	0.01676
1-Ethoxynaphthalene	do	do	0.01132

TABLE IV

Influence of different solvents on the Decomposition of 2-Methoxynaphthalene and 1-Methyl-2-Methoxynaphthalene. Decomposing agent, 1.5 c. cs. of constant boiling hydrobromic acid.

decomposing agent, 1.5 c. cs.of constant boiling hydrobromic acid.

Name of the ether	solvent	Mean velocity constant
2-Methoxynaphthalene	6 c.cs. of formic acid	0.05508
do	6 c.cs. of propionic acid	0·01056
do	6 c.cs. of butyric acid	0.007746
1-methyl-2-methoxynaphthalene	6 c.cs. of formic acid	0.03849
do	6 c.cs. of propionic acid	0.009166
do	6 c.cs. of butyric acid	0.007390

TABLE V

Influence of temperature on the decomposition of 2-methoxynaphthalene, 1-methyl-2-methoxynaphthalene and 1-chloro-2-methoxynaphthalene.

Solvent, 6 c.cs. of glacial acetic acid.

Decomposing agent, 1.5 c.cs. of constant boiling hydrobromic acid.

Name of the ether	Temperature	Mean velocity constant
2-Methoxynaphthalene	88°	0.006309
do	98°	0.01490
do	108°	0.03458
1-Chloro-2-methoxynaphthalene	88°	0.001272
do	98°	0.003597
do	108°	0.009385
1-Methyl-2-methoxynaphthalene	88°	0.004023
do	98°	0.01067
do	108°	0.02601

TABLE VI

Decomposition of Ethers by Alcoholic Caustic Potash.

In every case 0.001 mole of the ether is employed. Alcoholic caustic potash is prepared by dissolving 0.2800 grm. of caustic potash in 1.72 c.c. of ethyl alcohol.

Name of the ether	Temperature	Period of heating minutes	Ethyl alcoholic caustic potash	Percent decompositions in the results given are those obtained in the two duplicate experiments
2-Methoxynaphthalene	200°	300	2 c.cs.	56.56/51.78
2-Ethoxynaphthalene	200°	300	2 c.cs.	11.01/10.75
1-Methoxynaphthalene	200°	600	2 c.cs.	54.46/55.30
1-Ethoxynaphthalene	200°	600	2 c.cs.	15.77/15.01
Anisol	200°	960	2 c.cs.	40.33/39.67
Phenetol	200°	960	2 c.cs.	13.33/11.67

TABLE VII

2-Methoxynaphthalene	200°	180	2 c.cs.	27.72/26 26
1-bromo-2-methoxy-naphthalene	170°	120	2 c.cs.	54.17/51.48
1-Chloro—2-methoxy-naphthalene	170°	120	2 c.cs.	55.46/52.77

TABLE VIII

2-Methoxynaphthalene	200°	210	2 c.cs.	32.0/31.01
1-Methyl-2-methoxy-naphthalene	200°	210	2 c.cs.	23.54/20.25
1-Nitro-2-ethoxynaphthalene	130°	15	2 c.cs.	17.46/16.82

TABLE IX

1-Methoxynaphthalene	200°	420	2 c.cs.	29.25/27.28
4-Nitro-1-ethoxynaphthalene	100°	15	2 c.cs.	dirty decomposition products.
4-Nitro-1-ethoxynaphthalene	75°	10	2 c.cs.	2.84

VI—Discussion

(a) Influence of substituents on the decomposition of ethers and explanation suggested which accounts for it:—

An inspection of the results shows that under comparable conditions the velocity constants of the decomposition of unsubstituted ethers under the influence of halogen acids are in the following order:—

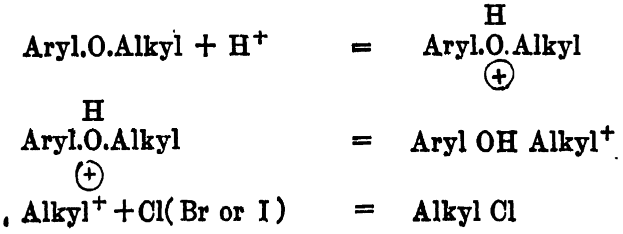
(1) β Naphthol ethers > α Naphthol ethers > phenolic ethers.

(2) Methyl ethers > Ethyl ethers.

(3) In ethers of substituted naphthols the velocity constants of the decomposition are smaller than those of the unsubstituted naphthol ethers. The influence of different substituents, in the ethers, on the decomposition velocity of these ethers is in the following order. Methyl > Bromine > Chlorine > Nitro.

An explanation depending upon the electronic behaviour of substituent groups in benzene nucleus may be advanced. Methyl group repels electrons while chlorine bromine, and NO_2 group attract them. The carbon atoms in position 2 and 4 counted from the carbon atom to which the substituent is attached become more negative or activated when the substituent is methyl and less negative or get deactivated when the substituent is chlorine bromine or nitro group. The substituents which enhance the nuclear activity are also found to facilitate a reaction in a side chain if the reaction depends upon the separation of a negative ion or the addition of a positive ion; conversely an electron attracting substituent retards a side chain reaction if it depends upon the separation of a positive ion or addition of a negative ion. (For an application of this principle called corresponding principle, refer to Oliver's work on the hydrolysis of substituted benzoyl chlorides. (Rec. Trav. Chem. *42*, 755, 1923 : *46*, 605, 1927).

The hydrolysis of phenolic ethers may be assumed to occur according to the following scheme.



$$\mathrm{Aryl.O.Alkyl} + H^{+} = \mathrm{Aryl.}\overset{H}{\underset{\oplus}{\mathrm{O}}}\mathrm{.Alkyl}$$

$$\mathrm{Aryl.}\overset{H}{\underset{\oplus}{\mathrm{O}}}\mathrm{.Alkyl} = \mathrm{Aryl\ OH\ Alkyl}^{+}$$

$$\mathrm{Alkyl}^{+} + \mathrm{Cl(Br\ or\ I)} = \mathrm{Alkyl\ Cl}$$

Methyl group repels electrons and makes the oxygen attached to the carbon in the 2 position more negative and thus facilitates the addition of the H ion. On the other hand with NO_2 group, as the drift of electrons is away from the nucleus, the addition of H is retarded and the velocity of the reaction becomes slower.

The course of the decomposition of Naphthol ethers with halogen acids can be represented by the same mechanism as that assumed above in phenyl ethers. The values of the velocity constants with chlorine, bromine and nitro substituents are much smaller than those of the unsubstituted naphthol ethers (instead of being greater as expected from the application of the above theory) are found to be smaller than those of the unsubstituted ethers. The influence of some factor still unknown may be responsible for this.

It is interesting to compare the velocity constants of the decomposition of the ethers of β naphthol and substituted β naphthols with the results obtained by Davis (J.C.S., 77, 32,1900) in the preparation of these ethers. The following table gives the results of Davis and the velocity constants of the decomposition of these ethers obtained in the present investigation

Methylation at 100° : Methyl alcohol, 2 grm.
Naphthol 2 grms., sulphuric acid, 0.80 grm.

Naphthol employed	Hours of heating	Percentage yield of ethers	Constants obtained in the present investigation
2-Oxynaphathalene	20	91.3	0.01391
1-Bromo-2-oxynaphthalene	20	21.0	0.003995
1-Chloro-2 oxynaphthalene	20	7.5	0.003025
1-Nitro-2-oxynaphthalene	20	—	0.0004828
1-6-dibromo-2-oxynaphthalene	20	5.4	0.002028

Ethylation at 100°: Ethyl alcohol, 2 grms.
Naphthol, 2 grms. Sulphuric acid, 0.80 grm.

Naphthol employed	Hours of heating	Percentage yield of ethers	Constants obtained in the present investigation
2-Oxynaphthalene	20	89.0	0.01261
1-Bromo-2-oxynaphthalene	20	17.0	0.003027
1-Chloro-2-oxynaphthalene	20	9.0	0.001977
1-Nitro-2-oxynaphthalene	20	—	0.0002991
1-6-dibromo-2-oxynaphthalene	20	6.0	0.001355

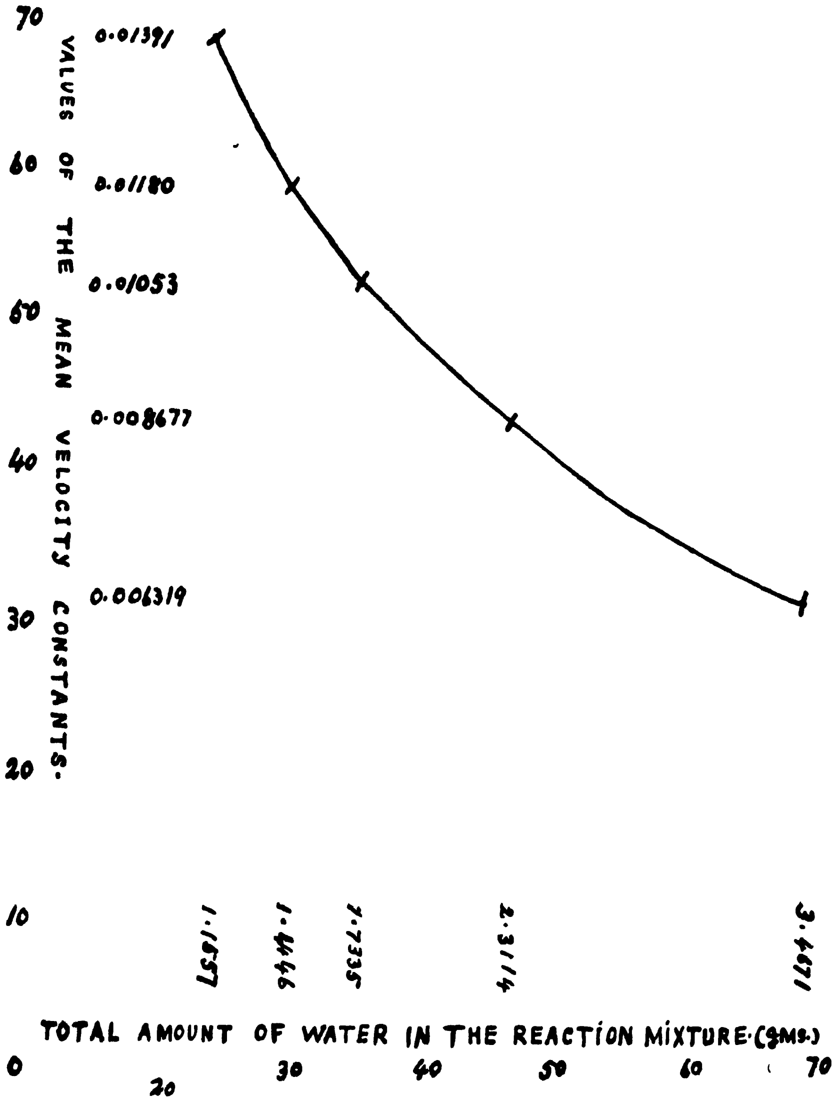
The substituents influence the formation and the decomposition in a similar way.

(b) *Influence of water in the reaction mixture on the velocity constant*:—

1.5 c.cs. of constant boiling hydrobromic acid already contains 1.1557 grms. of water. To study the influence of greater amounts of water on the reaction, experiments are done in which 0.288, 0.577, 1.155 and 2.311 grms. of water are added to the reaction mixture, the volume being kept constant by adjusting the amount of the solvent used. The velocity constants decrease as the amount of water in the reaction mixture increases as is shown in the accompanying graph.

(c) *Influence of halogen acids upon the decomposition of ethers under comparable conditions*:—

Table III gives the velocity constants of the decomposition of 2-methoxy, 2-ethoxy, 1-methoxy and 1-ethoxy naphthalene under comparable conditions. (The moles of halogen acid, ether, water and the total volume are kept the same). The velocity constants with hydrobromic acid in all cases are greater than those with hydrochloric acid and those with hydriodic acid are greater than those with hydrobromic acid. Thus the velocity of decomposition increases as the atomic weight of the halogen in the halogen acid increases,



Influence of Water on the decomposition of 2 Methoxy Naphthalene.

(d) *Influence of solvents on the velocity constants* :—

Table IV gives the values of the velocity constants with different solvents under comparable conditions. (moles of ether, halogen acid, water, and volume of the reaction mixture and temperature being kept constant.) The velocity constants with different acids as solvents are in the order :—

Formic acid > acetic acid > propionic > N-Butyric acid.

The dielectric constants of the different acids are :—

Formic acid	62.0
Acetic acid	7.0
Propionic acid	3.2
N-Butyric acid	2.9

The decrease in the dielectric constants is in the same order as the decrease in velocity constants, when these acids are employed as solvents. The dielectric constants of these solvents seem to be an important factor which influence the velocity of these reactions as was found by Menschutkin (Zeitsch, Physi. Chem. *6*, 41, 1890) who studied the reaction between ethyl iodide and triethyl amine in different solvents. He finds that the velocity constants are approximately proportional to the dielectric constants of the solvents employed.

(e) *Action of alcoholic caustic potash upon ethers* :—

Tables VII and VIII show that chlorine, bromine and nitro group substituted ethers decompose much more readily in the presence of alcoholic caustic potash than the unsubstituted ones. The influence is thus the reverse of that which these groups exert when the decomposition is brought about by halogen acids. Similar behaviour is observed by Tasman who studied (Rec. Trav. Chem. *46*, 653, 1927)) the influence of substituents on the opening of the Phthalide ring in an alkaline solution. The following are the velocities (referred to that of the unsubstituted phthalide as unity) obtained by him with different substituents in the 5th position (*i.e.*, meta to the carbonyl group.)

Cl	1.32
Br	1.53
NO_2	10.6

Thus Oliver's correspondence principle in an acid medium becomes an inverse correspondence in the example studied by Tasman in an alkaline medium.

The decompositions of methyl and ethyl ethers of α and β-naphthols and of their methyl, chloro, bromo and nitro derivatives by halogen acids in different solvents and by alcoholic caustic potash have been studied.

It is found that under comparable conditions the velocity constants of the ethers of β naphthol are higher than those of α naphthol. It is further found that methyl ethers decompose more rapidly than ethyl ethers.

In ethers of substituted naphthols the velocity constants depend on the nature of the substituted group or groups, on the nature of the decomposing agent employed, and on the nature of the medium. The velocity constants of ethers of substituted naphthols are smaller than those of the ethers of α and β naphthols. The influence of the different substituents on the velocity constants of ethers is :—

Methyl < Bromo < Chloro < Nitro

The velocity constants with hydriodic acid are greater than those with hydrobromic acid ; and those with hydrobromic acid are greater than those with hydrochloric acid.

The order of the velocity constants with different solvents (with hydrobromic acid as the decomposing agent) are :—

Formic acid > Acetic acid > Propionic acid > N. Butyric acid.

It is found that (unlike the decomposition with acids) chlorine, bromine and nitro substituted ethers decompose more rapidly than unsubstituted once, with alcoholic caustic potash as the decomposing agent.

An additive mechanism for the reactions occurring in the decomposition of ethers is suggested which to a certain extent explains the influence of substituents.

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STUDIES IN CHLORALAMIDES—PART V.

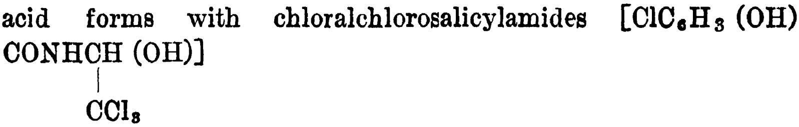
REACTIVITY OF HYDROXY GROUPS IN CHLORAL CHLORO-SALICYLAMIDES—II.

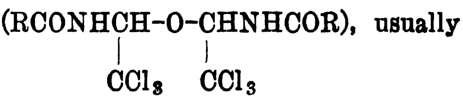
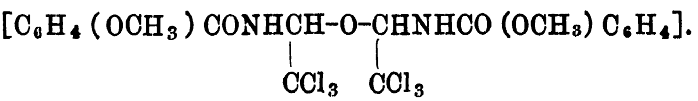
By

(The Late) N. W. HIRWE AND K. N. RANA

In continuation of the syntheses and constitution of chloralchlorosalicylamides the activities of the OH groups in the molecule are the subject of the present paper. It has been found earlier in Part I (Hirwe and (Miss) Gavankar, Jour. Univ. Bom. 1937, *6* (II), 123) that all the reactions affecting the side chain -OH group in the α-position also affect simultaneously the nuclear -OH group in chloralnitrosalicylamides.

Thus with chloral-3-chloro-, chloral-5-chloro-and chloral-3:5-dichlorosalicylamides, acetic anhydride, benzoyl chloride and dimethyl sulphate form diacyl and dialkyl derivatives respectively.

Acetic anhydride with a few drops of concentrated sulphuric acid forms with chloralchlorosalicylamides  $[ClC_6H_3(OH)\ CONH\underset{CCl_3}{\underset{|}{C}}H\ (OH)]$ diacetoxy derivatives $[ClC_6H_3\ (OCOCH_3).\ CONHCH\ (OCOCH_3)\ CCl_3]$. Similarly benzoyl Chloride and dimethyl sulphate give dibenzoyloxy and dimethoxy compounds.

Anhydrochloralamides  $(RCONH\underset{CCl_3}{\underset{|}{C}}H\text{-}O\text{-}\underset{CCl_3}{\underset{|}{C}}HNHCOR)$, usually obtained by the action of acetic anhydride or benzoyl chloride on a chloralamide in presence of alkali are obtained in the present case, when the nuclear-OH group of chloralsalicylamides is protected by methylation or otherwise. The methyl-ether of chloralsalicylamide when reacted as above forms the usual anhydro compound  $[C_6H_4\ (OCH_3)\ CONH\underset{CCl_3}{\underset{|}{C}}H\text{-}O\text{-}\underset{CCl_3}{\underset{|}{C}}HNHCO\ (OCH_3)\ C_6H_4]$.

Thus anhydro compounds have been obtained from chloral-5-chloro-2-methoxybenzamide and chloral-3:5-dichloro-2-methoxybenzamide.

EXPERIMENTAL

General Methods

Acetylation:—The chloralamide is heated, until a clear solution is obtained, with the necessary quantity of acetic anhydride and a few drops of concentrated sulphuric acid. The reaction mixture gives a solid on pouring in hot water which is further worked out.

Benzoylation:—The chloralamide is suspended in alkali (10% solution) and necessary quantity of benzoyl chloride is slowly added keeping the temperature down. Solid separated is filtered, washed free from alkali and worked out further.

Methylation:—Required quantity of dimethyl sulphate is added to the chloralamide suspended in alkali (10% solution) keeping the temperature down. The product of reaction separates as a solid or a paste which is worked further.

Anhydro Formation:—Necessary quantity of acetic anhydride when added to the chloralamide, except chloralsalicylamides, suspended in alkali (10% solution) yields a solid. This solid is further worked out and found to be an anhydro compound.

(1) *α—Acetoxychloral-3-chloro-2-acetoxybenzamide*:—

Prepared by acetylation, as described above, of chloral-3-chlorosalicylamide. The solid obtained was crystallised from alcohol: clusters of needles: m.p. 95–97°. No coloration with ferric chloride. (Found : Cl, 35.50 ; $C_{13}H_{11}O_5NCl_4$ requires Cl, 35.24 per cent.)

(2) *α-Methoxychloral-3-chloro-2-methoxybenzamide* :—

Prepared by methylation, as described above, of chloral-3-chlorosalicylamide. The pasty mass separated was filtered off and triturated with water, when a solid was obtained. It crystallised from alcohol : needles : m.p. 84–85°. No coloration with ferric chloride. (Found : Cl, 40.93 ; $C_{11}H_{11}O_3NCl_4$ requires Cl, 40.93 per cent.)

(3) *α-Acetoxychloral-5-chloro-2-acetoxybenzamide* :—

Prepared by acetylation, as described above, of chloral-5-chlorosalicylamide. The solid obtained was crystallised from alcohol; needles m. p. 143–144°. No coloration with ferric chloride. (Found : Cl, 35.24 ; $C_{18}H_{11}O_5NCl_4$ requires Cl, 35.24 per cent.)

(4) *α-Methoxychloral-5-chloro-2-methoxybenzamide* :—

(*a*) Prepared by methylation of chloral-5-chlorosalicylamide by the above method. The pasty mass separated was filtered off and triturated with water, when a solid was obtained. It crystallised from alcohol : needles : m.p. 131-132°. No coloration with ferric chloride. (Found : N, 4.05 ; Cl, 40.99 ; $C_{11}H_{11}O_3NCl_4$ requires, N. 4.03 ; Cl, 40.93 per cent.)

(*b*) Prepared by methylation of chloral-5-chloro-2-methoxybenzamide. The paste separated solidified on triturating with water. It crystallised from alcohol : needles : m.p. 131-132°. No coloration with ferric chloride. (Found : Cl, 41.06 ; $C_{11}H_{11}O_3NCl_4$ requires, Cl, 40.93 per cent.)

(5) *α-Acetoxychloral-3:5-dichloro-2-acetoxybenzamide* :—

Prepared by acetylation, as described above, of chloral-3:5-dichlorosalicylamide. The solid obtained crystallised from alcohol : needles : m.p. 142-144°. No coloration with ferric chloride. (Found : Cl, 40.62 ; $C_{13}H_{10}O_5NCl_5$ requires Cl, 40.57 per cent.)

(6) *α-Benzoyloxychloral-3:5-dichloro-2-benzoyloxybenzamide*:—

Prepared by benzoylation, as described above, of chloral-3:5-dichlorosalicylamide. The pasty mass separated solidified on triturating with dilute sodium carbonate solution. It cystallised from alcohol : minute needles : m.p. 110-112° with decomposition. No coloration with ferric chloride. (Found : Cl, 31.43 ; $C23H_{14}O_5NCl_5$ requires Cl, 31.61 per cent.)

(7) *α-Methoxychloral-3:5-dichloro-2-methoxybenzamide*:—

(*a*) Prepared from chloral-3:5-dichlorosalicylamide by methylation as described above. The pasty mass separated became solid on triturating with water. It crystallised from alcohol : white prisms : m.p. 102-103°. No coloration with ferric chloride. (Found : Cl, 46.36 ; $C_{11}H_{10}O_3NCl_5$ requires Cl, 46.52 per cent.)

(*b*) Prepared by methylation of chloral-3:5-dichloro-2-methoxybenzamide. The solid obtained crystallised from alcohol: white prisms : m.p. 102-103°. No coloration with ferric chloride. (Found : Cl, 46.41 ; $C_{11}H_{10}O_3NCl_5$ requires Cl, 46.52 per cent.)

(8) *α-Acetoxychloral-3-chloro-2-methoxybenzamide* :—

Prepared by acetylation of chloral-3-chloro-2-methoxybenzamide. The solid obtained crystallised from alcohol : white needles : m.p. 93-94°. No coloration with ferric chloride. (Found : Cl, 38.02 ; $C_{12}H_{11}O_4NCl_4$ requires Cl, 37.87 per cent.)

(9) *α-Acetoxychloral-5-chloro-2-methoxybenzamide* :—

Prepared by acetylation of chloral-5-choloro-2-methoxybenzamide. The solid obtained crystallised from alcohol: white needles: m.p. 124-125°. No coloration with ferric chloride. (Found: Cl, 37.84; $C_{12}H_{11}O_4NCl_4$ requires Cl, 37.87 per cent.)

(10) *α-Anhydrochloral-5-chloro-2-methoxybenzamide* :—

Prepared from chloral-5-chloro-2-methoxybenzamide by the above-described method. The solid obtained crystallised from alcohol: white prisms: m.p. 109-110°. No coloration with ferric chloride. (Found: Cl, 44.09; $C_{20}H_{16}O_5N_2Cl_8$ requires Cl, 43.82 per cent.)

(11) *α-Acetoxychloral-3:5-dichloro-2-methoxybenzamide* :—

Prepared by acetylation of chloral-3:5-dichloro-2-methoxybenzamide. The solid obtained crystallised from alcohol: needles: m.p. 153-154°. No coloration with ferric chloride. (Found: Cl, 43.14; $C_{12}H_{10}O_4NCl_5$ requires Cl. 43.35 per cent.)

(12) *α-Anhydrochloral-3:5-dichloro-2-methoxybenzamide* :—

Prepared from chloral-3:5-dichloro-2-methoxybenzamide by the above-described method. The solid obtained crystallised from alcohol: minute needles: m.p. 98-100°. No coloration with ferric chloride. . (Found: Cl, 49.84; $C_{20}H_{14}O_5N_2Cl_{10}$ requires Cl, 49.51 per cent.

Thanks are due to the Research Grant Committee of the University of Bombay for an award of a grant to one of the authors (N.W.H.), from which could be defrayed the part of the expenses.

Royal Institute of Science,
Bombay.

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BROMINATION OF ALIPHATIC KETONES

By

S. V. SHAH AND D. G. PISHAVIKAR

Direct bromination of ketones in the absence of catalysers with excess of bromine does not seem to have been attempted except in a few cases like acetone and diacetyl. Several ketones were brominated by us, the general method being to keep the ketones in contact with excess of bromine for four days at room temperature. Practically, in all the cases the reaction is accelerated after the absorption of the first portion of the bromine added. The bromine is added not all at once but in small portions. The absorption of the first portion of bromine takes in some cases about thirty to forty-five minutes. Once this absorption with evolution of vapours of hydrobromic acid has taken place, further absorption is accelerated till the requisite amount of bromine is absorbed. The reaction mixture is cooled from time to time in cold water bath. The remaining excess of bromine is added to the mixture and is kept for four days (at room temperature). After four days about three hundred c.c.s of water is added to the reaction mixture and the excess of bromine is removed by blowing air into the mixture. The heavy liquid bromocompound is separated by a separating funnel and the remaining traces of the excess of bromine are removed by distilling under reduced pressure. The resulting product, if liquid, is further distilled under reduced pressure and if solid, is fractionally crystallised using ether as solvent. In measuring the yields the purified products were taken into account and not the raw products.

The results are given in a tabular form:

No.	Name of the Ketone Gms.	Bromine added, Gms.	Bromo-ketone Yield, Gms.
1.	Acetone.[1] $CH_3CO.CH_3$ 11 gms.	192 gms.	C_3HOBr_5 25 gms.
2.	Methylethylketone.[2] $CH_3CO.CH_2CH_3$ 8 gms.	150 gms.	$C_4H_4O.Br_4$ 19 gms.
3.	Diethylketone.[3] $C_2H_5CO.C_2H_5$ 8 gms.	160 gms.	$C_5H_7O.Br_3$ 26 gms.
4.	Dipropylketone $C_3H_7CO.C_3H_7$ 7 gms.	145 gms.	$C_7H_{11}O.Br_3$ 17 gms.
5.	N-Dibutylketone $C_4H_9CO.C_4H_9$ 14 gms.	290 gms.	$C_9H_{15}O.Br_3$ 25 gms.
6.	Iso-dibutylketone $\left.\begin{array}{l}(CH_3)_2CH.CH_2\\(CH_3)_2CH.CH_2\end{array}\right>CO$ 10 gms.	208 gms.	C_9H_1[illegible]$O.Br_3$ 19 gms.
7.	Capron $\left.\begin{array}{l}CH_3(CH_2)_4\\CH_3(CH_2)_4\end{array}\right>CO$ 11 gms.	235 gms.	$C_{11}H_{19}O.Br_3$ 17 gms.
8.	Diacetyl[4] $CH_3CO.CO.CH_3$ 17 gms.	195 gms.	$C_4H_2O.Br_4$ 48 gms.
9.	Acetonylacetone[5] $CH_3CO.CH_2CH_2CO.$ CH_3 10 gms.	150 gms.	$C_6H_2O.Br_8$ ...
10.	Pinacolin[6]. $CH_3CO.C(CH_3)_3$ 5 gms.	100 gms.	$C_6H_{10}O.Br_2$ 8.6 gms.

Yield.	M.P.	B.P. at ordinary pressure.	B.P. at 4 mm pressure.	Analysis						Remarks.
				Found.			Required.			
				C	H	Br	C	H	Br	
1 28 per cent.	72°–73°c	......	......	8.13% 7.95%	0.28% 0.29%	88 01% 88.40%	7.93%	0.22%	88.30%	
2 44%	54°c	......	......	...	...	82.4%	...	...	82.47%	Prepared for the first time by direct bromination
3 81%	...	231°c-233°c Decomposes	90°-93°c	18.31% 18.58%	2.05% 2.24%	73.77% 73.50%	18.50%	2.16%	74.30%	„
4 78%	...	219°-221°c Decomposes	120°-123°c	23.39%	3.05%	68.78% 67.75%	23.9%	3.13%	68.30%	Prepared for the first time.
5 65%	...	182°c-185°c without decomposition	121°-123°c	...	...	63.09% 62.77%	...	...	63.32%	„
6 70%	...	Decomposes at 195°c	129°-132°c	...	...	63.21% 62.83%	...	...	63.32%	„

7	65%	...	215°-218°c Decomposes.	162°-165°c	...	...	58.54% 58.20%	...	...	58 96%	Prepared for the first time.
8	60%	94°c	...	...	...	...	...	...	...	...	Analysis is not done as the melting point is the same as that of a similar compound described in literature.
9	...	181°c	...	...	...	...	84.75% 85.05%	...	...	85.79%	Prepared for the first time.
10	66%	68°c	...	...	...	...	61.89% 62.32%	...	...	62.01%	Prepared for the first time by direct bromination.

1. Beilstein. Vol. I. pp. 659. Mulder, J. *1864*, 330; Steiner, B. *7*, 505, 1284; Grimaux. Bl (2) *22*, 22. 12 parts bromine to one part acetone give a bromoderivative $C_3H.O.Br_5$. M.P. 72°c.
2. „ „ „ „ 670. Pastureau, *c.* r. *143*, 968; *144*, 92; Bl (4), *5*, 226, Methylethylketonesuperoxide $(C_4H_8O_2)_2$ and bromine give in the presence of water a bromoderivative $C_4H_4O.Br_4$.
3. „ „ „ „ 681. Pastureau, Bl (4). *5*, 226. Diethylketonesuperoxide $(C_6H_{10}O_2)_2$ and bromine give a bromoderivative $C_6H_7O.Br_3$. B.P. 142°c at 100 mm pressure.
4. „ „ „ „ 774. Keller, B. *23*, 35. By heating diacetyl in CS_2 with excess of bromine a bromo derivative $C_4H_2O.Br_4$. is obtained. M.P. 95-° 96°c
5. In this case, bromination is carried out in the presence of water and the reaction mixture is cooled in ice from time to time. If the reaction is carried out without the presence of water it becomes so vigorous that a resinous product is obtained.
6. Beilstein Supplementary Vol. I. pp. 357. Richard, Langlais, Bl (4) *7*, 467

All the bromoketones described above are soluble in ether, alcohol, benzene and less soluble in water; they have a penetrating odour attacking the eyes.

All the ketones (except, di-acetyl, acetonyl acetone, methyl ethyl ketone and penacoline) used in this investigation were prepared in this laboratory by heating the calcium salts of the corresponding acids, which is the general method for the preparation of all the ketones in general.* Diacetyl, acetonyl acetone, methyl-ethyl ketone and pinacoline were obtained from chemischefabrik. Dr. Theodor Schuchardt, G. M. B. H. Görlitz, Germany.

From the results given in the table it can be seen that irrespective of the length of the chain and the number of hydrogen atoms, even in the presence of excess of bromine, only a few of the hydrogen atoms are replaced by bromine. In the case of compounds containing more than one-CO-group the number of hydrogen atoms replaced by bromine is much greater. On examining the constitutional formulæ of the original ketones, one can observe the following:—

The number of hydrogen atoms replaced by bromine is equal to the number of hydrogen atoms (attached to the carbon atoms, adjacent to the -CO-group or groups) less the number of -CO-groups present. The following empirical formula is tentatively suggested to explain the results obtained:

$$h=H-C$$

where 'h' indicates the number of hydrogen atoms replaced by bromine, 'H' indicates the total number of hydrogen atoms attached to the carbon atoms, adjacent to the-CO-group or groups, and 'C' indicates the number of-CO-groups present in the compounds. For instance No. 9 has two-CO-groups with ten hydrogen atoms attached to the carbon atoms adjacent to the -CO-group. Thus in the equation, $h=H-C$, substituting the values of 'H' (1C) and C (2) we get the value h=8, and in fact

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*Diethylketone...Beilstein Vol. I pp. 679. Morley. A. *78*, 187; (this worker used barium propionate whereas we used calcium propionate).

N-dipropylketone...Beilstein Vol. I. pp. 699. Chanel, A. *52*, 295;

N-*dibutylketone*...Beilstein suppl. Vol. I. pp. 365. Sabatier, Mailhe, Cr. *156*, 1731. (this method of preparation was slightly modified inasmuch as we merely distilled the calcium salts, whereas these authors passed the acid vapours over heated calcium carbonate.

Iso-dibutylketone...Beilstein Vol. I. pp. 710. Dilthey, A. *318*, 169. B. *34*, 2116.

Capron...Beilstein Vol. I. pp. 714. Schmidt, B. *5*, 601; Lieben, Janecek, A. *187*, 134.

only eight hydrogen atoms have been replaced by bromine. In the same way the equation can be verified for the remaining nine compounds.

However, we are of the opinion that some more ketones must be studied to make the equation finally acceptable. We are studying a few more ketones from this point of view.

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CONDENSATION OF SUCCINIC ANHYDRIDE WITH PHENOLS.

By

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Ullman and Schmidt (Ber. 1919, *52*, 2098.) showed that free phenols could be condensed with the anhydride of a dibasic acid by Friedel and Craft's reaction provided acetylene tetrachloride is used as solvent. Mitter and De (J. Ind. Chem. Soc. 1935, 747.) condensed phenol with succinic anhydride and obtained β-o-hydroxybenzoylpropionic acid identical with the acid prepared by Rosenmond and Schapiro (Arch. Pharm. 1934, *272*, 313.). We have now condensed succinic anhydride with phenol and isomeric cresols. It was found that the reaction proceeded only when acetylene tetrachloride was used as solvent and the temperature of the reaction mixture was between 120°-135°. The use of nitrobenzene as a solvent at high temperature was unsatisfactory as it gave much tarry matter accompanied by small quantities of condensation products.

Phenol when condensed with succinic anhydride gave two products which could be separated by crystallisation from boiling water. The less soluble product, which forms more than 90 per cent of the total condensation product, had m.p. 146° and was identified as β-o-hydroxybenzoylpropionic acid (Rosenmond and Schapiro loc. cit.). On methylation it gave *β-o-methoxybenzoylpropionic acid*, m.p. 97°, identical with the substance synthesised from o-methoxybenzoyl chloride and ethylacetosuccinate following the keto ester synthesis of Mrs. Robinson (J. C. S. 1930, 745.) The constitution of the other product was proved to be *βp-hydroxybenzoylpropionic acid* as it gave on methylation a product identical with βp-methoxybenzoylpropionic acid of Rosenmond and Schapiro (loc. cit.). o-cresol when condensed with succinic anhydride gave two products which could be separated by nitrobenzene. The substance less soluble in nitrobenzene had m.p. 184° and was proved to have the constitution *β4-hydroxy-3-toluoylpropionic acid* as it gave on methylation β-4-methoxy-3-toluoylpropionic acid of Rosenmond and

Schapiro (loc. cit.) The other product recovered from nitrobenzene had m.p. 136°-137°. Its constitution *viz. β-2-hydroxy-3-toluoylpropionic acid* follows from the following facts. (1) It gave a bluish colouration with alcoholic ferric chloride, thus indicating that the side chain -$COCH_2CH_2COOH$ is in ortho position to the hydroxyl group. (2) The hydroxyl group in the substance could not be methylated by dimethyl sulphate and sodium hydroxide solution under any conditions. This is no doubt due to steric hindrance.

m-cresol gave two products which could be separated by water. The less soluble product which forms about 95 per cent of the total condensation product had m.p. 154°. It gave a bluish colouration with alcoholic ferric chloride and on methylation gave a methoxy acid m.p. 118°, thus indicating that the condensation had not taken place in the para position to the hydroxyl group since β4-methoxy-2-toluoylpropionic acid has m.p. 136°. (Rosenmond and Schapiro. loc. cit.) Oxidation of the methoxy acid did not give any crystalline product. The constitution of the acid m.p. 154° is thus somewhat uncertain and is assumed to be *β-2-hydroxy-4-toluoylpropionic* acid. The more soluble product had m.p. 172° and was shown to have the constitution *β-4-hydroxy-2-toluoyl-propionic* acid as it was identical with the substance obtained by demethylating β-4-methoxy-2.toluoylpropionic acid of Rosenmond and Schapiro.

p-cresol gave only one product which was found to be identical with β 2-hydroxy-5-toluoylpropionic acid of Rosenmond and Schapiro.

EXPERIMENTAL

General procedure for the condensation of phenols with succinic anhydride :—Anhydrous aluminum chloride (28 gms) was added in two lots to a mixture of phenol (0.1 mol) succinic anhydride (0.1 mol.) and acetylene tetrachloride (75 gms) kept in a round bottomed flask carrying a calcium chloride tube. It was then refluxed in an oil bath at 120°-130° for two hours, decomposed with ice and hydrochloric acid and distilled with steam to remove the solvent and the unused phenol. The solid obtained on cooling was extracted with a solution of sodium carbonate, boiled with the addition of animal charcoal, filtered and the product recovered by acidification. The filtrate was concentrated to recover the more soluble product in some cases. The yields are given in the following table.

Phenol used.	Products obtained.	Approximate per cent yields.
Phenol.	1. β-o-hydroxybenzoylpropionic acid	30–35 per cent.
	2. β-p-hydroxybenzoylpropionic acid	2–3 per cent.
o-cresol.	1. β-2-hydroxy-3 toluoylpropionic acid.	35–40 per cent.
	2. β-4-hydroxy-3 toluoylpropionic acid.	15–20 per cent.
m-cresol.	1. β-2-hydroxy-4-toluoylpropionic acid.	60–65 per cent.
	2. β-4-hydroxy-2-toluoylpropionic acid.	1–2 per cent.
p-cresol.	β-2-hydroxy-5-toluoylpropionic acid.	40–45 per cent.

β-o-hydroxybenzoylpropionic acid crystallised from hot water in woolly needles m.p. 146°. (Found C,61.8 H,5.4 per cent. Ag in the silver salt, 35·4 per cent. Calculated for $C_{10}H_{10}O_4$ C,61·9; H, 5.4. per cent. $C_{10}H_9O_4Ag$ requires Ag, 35·9 per cent.) *Ethyl-βo-hydroxybenzoylpropionate* prepared by Fischer Speier method was a colourless liquid b. p. 255 at 184 mm. (Found C,64.7; H,6.5, per cent. $C_{11}H_{14}O_4$ requires C,64.9;H,6.3 per cent.) *βo-methoxybenzoylpropionic acid* obtained by methylating the above acid crystallised from hot water in needles m.p. 97°–98° and was identical with the acid synthesised as described below. Synthesis of βo-methoxybenzoylpropionic acid by Mrs. Robinson's method:- Ethylacetosuccinate (22 gms) was added to finely divided sodium (2.3 gms) suspended in dry ether (100 c.c.). After all sodium had dissolved o-methoxybenzoyl chloride (17 gms.) was added and warmed on the water bath. The product recovered by acidification was hydrolysed in cold by four per cent potassium hydroxide solution for 24 hours. The substance was recovered and further hydrolysed by boiling with five per cent sulphuric acid for four hours. It was soluble in the usual solvents and had m.p. 97° (Found C,63.1; H,5.8 per cent, Eq.Wt,209.0 $C_{11}H_{12}O_4$ requires C,63.5; H,5.8 per cent Eq. Wt, 208.0.)

β-p-hydroxybenzoylpropionic acid was soluble in water, alcohol, acetic acid and in hot ethyl acetate but insoluble in petrol, benzene and chloroform. It crystallised from ethyl acetate in flat needles m.p.156°. (Found C,61.7; H,5.5 per cent. $C_{10}H_{10}O_4$ requires C,61.9; H,5.4. per cent.) *Ethyl-β-p-hydroxybenzoylpropionate* was a colourless solid m.p.111°. (Found C,64.7; H,6.6. per cent. $C_{12}H_{14}O_4$ requires C,64.9; H,6.3. per cent.)

Separation of the two products from the condensation of o-cresol:-The product was warmed with five times its quantity of nitrobenzene till a clear solution resulted. On cooling β 4-hydroxy-3-toluoylpropionic acid separated. It was filtered and washed with petrol to remove nitrobenzene. The other product was recovered from the filtrate by removing nitrobenzene by steam distillation.

β-4-hydroxy-3-toluoylpropionic acid was soluble in hot water and alcohol, slightly soluble in hot ethyl acetate and insoluble in benzene, chloroform and petrol. It crystallised in needles from water m.p. 184° and did not give any colour with ferric chloride. (Found C,63.3; H,5.8 per cent. Ag. in silver salt, 33.9 per cent. $C_{11}H_{12}O_4$ requires C,63.5; H,5.8 per cent. $C_{11}H_{11}O_4Ag$ requires Ag,34.2 per cent.) *Methyl β4-hydroxy-3-toluoylpropionate* crystallised from ethyl acetate and petrol in needles m.p.108° (Found C,64.7; H, 6.6 per cent. $C_{12}H_{14}O_4$ requires C,64.9; H,6.3 per cent.) *Ethyl β4-hydroxy-3-toluoylpropionate* crystallised from benzene and petrol had m.p. 106° and depressed the m.p. of the methyl ester. (Found C,65.9; H,6.7 per cent. $C_{13}H_{16}O_4$ requires C,66.1; H,6.8 per cent.)

β-2-hydroxy-3-toluoylpropionic acid was soluble in alcohol, ethyl acetate and acetic acid but insoluble in petrol. It crystallised from water or benzene in long needles m.p. 136°-137° and gave bluish colour with ferric chloride. (Found C,63.3 ; H,5.5 per cent. Eq. Wt,210.0. $C_{11}H_{12}O_4$ requires C,63.5; H,5.8 Eq. Wt,208.) *Methyl β-2-hydroxy-3-toluoylpropionate* had m.p. 78°. (Found C,64.6 ; H,6.6 per cent. $C_{12}H_{14}O_4$ requires C,64.9 ; H,6.3 per cent.) *Ethyl β-2-hydroxy-3-toluoylpropionate* had also m.p. 78° but depressed the m,p. of the methylester. (Found C,65.8 ; H,6.8 per cent. $C_{13}H_{16}O_4$ requires C,66.1; H,6.8 per cent.)

β2-hydroxy-4-toluoylpropionic acid was slightly soluble in cold in the usual solvents and crystallised from alcohol in stout rods or prisms. m.p.154°. and gave a bluish colour with ferric chloride. (Found C,63.4; H, 5.9 per cent. $C_{11}H_{12}O_4$ requires C,63.5; H,5.8 per cent.)

β 4-hydroxy-2-toluoylpropionic acid was soluble in alcohol ethyl acetate and in hot water from which it crystallised in short needles. m.p.172°. and gave no colour with ferric chloride. (Found C,63.3; H,5.5 per cent $C_{11}H_{12}O_4$ requires C,63.5; H,5.8 per cent.) An identical acid was obtained by heating β4- methoxy-2-toluoylpropionic acid of Rosenmond and Schapiro ith anhydrous aluminum chloride at 150°.

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A NOTE ON THE HŒSCH CONDENSATION WITH ETHYLENE DICYANIDE

By

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With a view to prepare β-dihydroxy-benzoyl propionic acids attempts were made to condense succinic anhydride with dihydric phenols following the method of Raval, Bokil and Nargund. (see preceding paper). It was, however, found that the reaction was very complicated, highly coloured products being formed in each case. It was not possible to isolate β-dihydroxy-benzoyl propionic acids. β-2-4-dihydroxy-benzoyl propionic acid has been already prepared by Murai by Hœsch condensation of ethylene dicyanide with resorcinol. (Bull. Chem. Soc. Japan. *I*, 129; Science Report of Tohoku Imperial University, 1926, *15*, 675). It was thought that other phenols might behave similarly and yield the desired keto acids. Attempts were, therefore, made to condense etylene dicyanide with phenol, isomeric cresols, resorcinol, resorcinol monomethyl ether, catechol, hydroquinone, orcinol and pyrogallol. It was found that, except resorcinol and resorcinol monomethyl ether, none condensed with ethylene dicyanide. The m.p. of β-2-4-dihydroxy-benzoyl propionic acid was 205°. Murai gives 199–200°. Murai stated that β-2-4-dihydroxy-benzoyl propionic acid on methylation gave β-2-4-dimethoxy-benzoyl-propionic acid m.p. 124°–125°. It was found that β-2-4 dihydroxy-benzoyl propionic acid on methylation with dimethyl sulphate in molecular proportions gave β-2-hydroxy-4-methoxy-benzoyl propionic acid m.p. 156°, and on further methylation gave β-2-4-dimethoxy-benzoyl propionic acid m.p. 148° identical with the products described by Dalal and Nargund. (Jour. Ind. Chem. Soc. 1937, *14*, 406). Resorcinol monomethyl ether gave β-2-hydroxy-4-methoxy-benzoyl propionic acid. β-2-4-dihydroxy-benzoyl propionic acid has been characterised by the preparation of methyl ester m.p. 138° and ethyl ester m.p. 100°.

EXPERIMENTAL.

Resorcinol (0·1 mol). and ethylene dicyanide (0·1 mol). were dissolved in dry ether (75 c. c.) and the solution cooled in a freezing mixture. Anhydrous zinc chloride (2 gms.) was added and dry hydrogen chloride was passed for four hours. It was then decomposed with cold water (50 c. c.), the ether layer removed and the aqueous layer heated on water bath for half an hour. The solid obtained on cooling was filtered and crystallised from water (yield 4 gms). β-2-4-dihydroxy-benzoyl-propionic acid (needles from water) was soluble in methyl and ethyl alcohol but insoluble in benzene, petrol and chloroform and had m.p. 205°. Ba and Ca salts were soluble while Pb and Ag salts were insoluble in water. (Found :—C, 56·82 H,4·93 per cent. calculated for $C_{10}H_{10}$, O_5: C, 57·14 H, 4·76 per cent).

Methyl β-2-4-dihydroxy-benzoyl-propionate prepared in the usual manner was soluble in alcohol and hot water but insoluble in benzene, petrol, chloroform and ethyl acetate. It crystallised from dilute alcohol in small needles and had m.p. 138°. (Found C, 58·72 H, 5·51 per cent. $C_{11}H_{12}O_5$ requires C, 58·94 H, 5·36 per cent.)

Ethyl β-2-4-dihydroxy-benzoyl-propionate was soluble in hot water and hot ethyl acetate and insoluble in petrol and chloroform. It crystallised from ethylacetate and petrol in tiny needles and had m.p. 100°. (Found C, 60·41 H, 6·00 per cent. $C_{12}H_{14}O_5$ requires C, 60·50 H, 5·88 per cent.)

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CONDENSATION OF MALEIC ANHYDRIDE WITH PHENOLIC ETHERS

By

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Maleic anhydride has been condensed by Friedel and Craft's reaction with benzene, toluene and anisole, and β benzoyl acrylic acid, β p-methyl-benzoyl acrylic acid and β p-methoxy-benzoyl acrylic acids have been obtained. (Pechmann. Ber. 1882, *15*, 881. Gabriel and Coleman Ber. 1899, *32*, 397. Rice J. A. C. S. 1923, *45*, 228. *ibid*, 1924, *46*, 218.). Rice (J. A. C. S. 1931, *53*, 3153) condensed maleic anhydride with resorcinol dimethyl ether with a view to get β 2-4-dimethoxy-benzoyl-acrylic acid. This acid was obtained by him in small quantity and, in addition, he isolated two other products from this reaction *viz.* (1) 2-4-dimethoxy-phenyl succinic anhydride which formed the main product and (2) α 2-4-dimethoxy-phenyl β 2-4-dimethoxy-benzoyl propionic acid. The formation of the latter substance was ascribed to the addition of resorcinol dimethyl ether to β 2-4-dimethoxy-benzoyl acrylic acid. As methoxy-phenyl succinic acids were required in this laboratory in connection with work on synthetical anthelmintics it was thought that other phenolic ethers might behave in a manner similar to resorcinol dimethyl ether and give the corresponding succinic acids by condensation with maleic anhydride. A systematic investigation of the condensation of maleic anhydride with anisole, isomeric cresol methyl ethers, veratrole, and hydroquinone dimethyl ether has been carried out. It was found that in all cases an unsaturated keto acid was the sole product of the reaction no corresponding succinic acid being obtained. It is also remarkable that in no case was there an addition of the phenol ether to the keto unsaturated acid. It, therefore, appears that resorcinol dimethyl ether is the only compound which gives the corresponding succinic acid.

The unsaturated keto acids were characterised by the preparation of methyl and ethyl esters and bromine addition products. In case of the bromine addition products no evolution of hydrobromic acid was detected and in all cases the compounds obtained contained two bromine atoms. The constitutions of the acids were established by oxidation.

EXPERIMENTAL

General procedure for the condensation of phenol ethers with maleic anhydride :—Anhydrous aluminum chloride (28 gms) was added gradually to a mixture of maleic anhydride (0.1 mol), phenol ether (0.1 mol) and the solvent (100 c.c.) kept in a round bottomed flask carrying a calcium chloride tube. Care was taken to see that no rise of temperature higher than 40° took place. After four hours at ordinary temperature it was decomposed with ice and hydrochloric acid and steam distilled to remove the solvent and the unused phenol ether. The solid obtained on cooling was filtered, washed with cold water and extracted with a dilute solution of sodium carbonate. The extract was boiled with the addition of animal charcoal, filtered and acidified. The yields obtained are given in the following table.

Phenol ether used	Product obtained	Per cent yield.
anisole	β p-methoxy-benzoyl-acrylic acid.	54 per cent, in carbondisulphide.
o-cresol methyl ether	β *3-methyl-4-methoxy-benzoyl-acrylic acid*	100 per cent, in nitrobenzene.
m-cresol methyl ether	β *2-methyl-4-methoxy-benzoyl-acrylic-acid*	92 per cent, in nitrobenzene.
p-cresol methyl ether	β *2-methoxy-5-methyl-benzoyl-acrylic acid*	82 per cent, in nitrobenzene and 70 per cent in carbondisulphide.
Veratrole	β *3-4-dimethoxy-benzoyl-acrylic acid.*	50 per cent, in nitrobezene and 46 per cent in CS_2

P-methoxy-benzoyl acrylic acid :—It was soluble in methyl and ethyl alcohol, acetic acid, and ethyl acetate, slightly soluble in benzene, chloroform, hot water and insoluble in petrol. It crystallised from hot water in faintly yellow woolly needles and had m.p. 129°. It formed a methyl ester m.p. 64° and an ethyl ester m.p. 47°. Rice (J. A. C. S. 1924, 218) who has already prepared these compounds gives the m.p. as under. β p-methoxy-benzoyl acrylic acid m.p. 130 methyl β p-methoxy-benzoyl acrylate m.p 62° and ethyl β p-methoxy-benzoyl acrylate m.p. 47°.

β 3-methyl-4-methoxy-benzoyl acrylic acid:—It was soluble in methyl and ethyl alcohol, ethyl acetate, benzene, chloroform and acetic acid and insoluble in water and petrol. It crystallised from alcohol in yellowish prismatic needles and had m.p. 163°. Ba and Ca salts were soluble while Pb and Ag salts were insoluble in water. (Found C, 65.37 H, 5.51 per cent., Equit Wt, 217; $C_{12}H_{12}O_4$ requires C, 65.46 H, 5.45 per cent Eq. Wt. 220.)

Oxidation of β 3-methyl-4-methoxy-benzoyl acrylic acid:— To a solution of the acid (2 gms) in a small quantity of sodium hydroxide solution was added potassium permanganate (6.5 gms) dissolved in water (300 c.c.). The oxidation was complete at ordinary temperature in half an hour. It was then warmed, excess of potassium permanganate destroyed by addition of alcohol, filtered, the filtrate concentrated and acidified. The product obtained had m.p. 190° and was identified as 3-methyl-4-methoxy-benzoic acid. (Schall Ber. *12*, 825.)

Methyl β 3-methyl-4-methoxy-benzoyl acrylate prepared by esterifying the above acid by Fischer Speier method was a colourless solid m.p. 106°. It was soluble in the usual solvents and crystallised from alcohol in needles. (Found C, 66.39 H, 6.22 per cent $C_{13}H_{14}O_4$ requires C, 66.66 H, 5.98 per cent.)

Ethyl β 3-methyl-4-methoxy-benzoyl acrylate prepared similarly had m.p. 60°. Found C, 67.63 H, 6.66 per cent. $C_{14}H_{16}O_4$ requires C,67.72 H, 6.45 per cent.)

αβ dibromo β 3-methyl-4-methoxy-benzoyl propionic acid. This was obtained by adding theoretical quantity of bromine dissolved in carbondisulphide to a solution of the acid in CS_2. It crystallised from dilute acetic acid in colourless needles and had m. p. 122°. (Found Br, 42.32 per cent Eq. wt., 382.$C_{12}H_{12}O_4Br_2$ requires Br, 42.10 per cent. Eq. Wt, 380.)

β 2-methyl-4-methoxy-benzoyl-acrylic acid:—It was easily soluble in alcohol, ethyl acetate, chloroform, hot water and hot benzene. It crystallised from water in short yellow needles m. p 141°. (Found C, 65.23 H, 5.55 per cent. $C_{12}H_{12}O_4$ requires C, 65.46 H, 5.45 per cent. Eq. Wt. 220). On oxidation it gave 2-methyl-4-methoxy-benzoic acid m. p. 176°. *Ethyl β 2-methyl-4-methoxy-benzoyl acrylate* was a liquid b. p. 209 at 11 mm. (Found C, 67.56 H, 6.72 per cent. $C_{14}H_{16}O_4$ requires C,67.72

H,6.45 per cent.) The methyl ester and bromine addition products were obtained as thick red oils which could not be purified.

β 2-methoy-5-methyl-benzoyl acrylic acid:—It was soluble in alcohol, ethyl acetate, chloroform, benzene and hot water. It crystallised in pale yellow needles m. p. 126°. (Found C,65.37 H, 5.63 per cent. Eq. Wt, 222.7. $C_{12}H_{12}O_4$ requires C, 65.46 H, 5.45 per cent. Eq. Wt., 220). It gave on oxidation 2-methoxy-5-methyl-benzoic acid m. p. 68°. *Ethyl β 2-methoxy-5-methyl-benzoyl acrylate* was a colourless liquid b. p. 197° at 17 mm. (Found C, 67.63 H, 6.5 per cent. $C_{14}H_{16}O_4$ requires C, 67.72 H, 6.45 per cent). *αβ dibromo β 2-methoxy-5-methyl-benzoyl propionic acid* crystallised from acetic acid in colourless needles m. p. 141°. (Found Br, 42.44 per cent $C_{12}H_{12}O_4Br_2$ require Br, 42.10 per cent).

β 3-4-dimethoxy-benzoyl acrylic acid:—It was soluble in alcohol, ethyl acetate, acetic acid and hot water but insoluble in benzene. It crystallised from hot water in square plates m. p. 178°. (Found C, 60.85 H, 5.13 per cent. Eq. Wt. 235.6 $C_{12}H_{12}O_5$ requires C, 61,03 H. 5.08 per cent Eq. Wt, 236). On oxidation it gave veratric acid m. p. 179°. *Methyl β 3-4-dimethoxy-benzoyl acrylate* crystallised from alcohol in pale-yellow needles m. p. 91°. (Found C, 62.13 H, 5.61 per cent. $C_{13}H_{14}O_5$ requires C, 62.40 H, 5.61 per cent). *Ethyl β 3-4-dimethoxy-benzoyl acrylate* was a colourless liquid b. p. 115 at 22 mm. (Found C, 63.51 H, 6.23 per cent. $C_{14}H_{16}O_5$ requires C, 63.63 H, 6.06 per cent.) *αβ dibromo β 3-4-dimethoxy-beuzoyl propionic acid* crystallised from acetic acid in microscopic crystals m.p. 203°. (Found Br, 40.21 per cent. Eq. Wt, 392. $C_{12}H_{12}O_5Br_2$ requires Br, 40.40 per cent Eq. Wt, 396).

β 2-5-dimethoxy-benzoyl acrylic acid:—It was soluble in alcohol chloroform, benzene, acetic acid and hot water but insoluble in petrol. It crystallised in reddish needles from water Ba and Ca salts were soluble while Ag, and Pb salts were soluble in hot water. (Found. C, 60.68 H, 5.13 per cent. Eq. Wt, 231. $C_{12}H_{12}O_5$ requires C, 61.03 H, 5.08 per cent. Eq. Wt, 236). On oxidation it gave 2-5-dimethoxy benzoic acid m. p. 77°. *Methyl β 2-5-diMethoxy benzoyl acrylate* was a liquid b. p. 216 at 42 mm. It solidified after sometime and had m. p. 65°. (Found C, 62.28 H, 5.73 per cent. $C_{13}H_{14}O_5$ requires C, 62.40 H, 5.60 per cent). *Ethyl β 2-5-dimethoxy-benzoyl acrylate* was a yellow oil b. p. 175° at 22 mm. (Found C, 63.56 H, 6.17 per cent, $C_{14}H_{16}O_5$ requires

C, 63.63 H, 6.06 per cent). *αβ dibromo β 2-5-dimethoxy-benzoyl propionic acid* crystallised in colourless needles m. p. 45°. (Found Br. 40.55 per cent Eq. Wt, 395. $C_{12}H_{12}O_5Br_2$ requires Br, 40.40 per cent. Eq. Wt, 396).

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HYDROXY AND METHOXY PHENYL SUCCINIC ACIDS

By

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Hydroxy or methoxy phenyl succinic acids are required in this laboratory in connection with work on synthetical anthelmintics. At present the following are known:—o-hydroxy-phenyl succinic acid (Bredt and Kallen Ann. 1896, *293*, 366), p-methoxy-phenyl succinic acid (Baker and Lapworth J. C. S. 1925, 560), p-hydroxy-phenyl succinic acid (Chrzaszczewska, Roczniki. Chemji. 1925, *5*, 1-3. 33–76). and 2-4-dimethoxyphenyl succinic acid (Rice J. A. C. S. 1931, *53*, 3153). Of these the chemistry of p-hydroxy-phenyl succinic acid is very little known. The preparation of o-methoxy, m-hydroxy, m-methoxy and p-hydroxy-phenyl succinic acids is described in the present communication.

The very general method of Hisgon and Thorpe (J. C. S. 1906, 1455) for the preparation of substituted succinic acids is however, not a convenient one in the present case as the cyanohydrins of hydroxy phenyl aldehydes are difficult to prepare. The excellent method of Lapworth and Collaborators is applicable in the present case. (J. C. S. 1922, 49, 1699, 2741. *ibid.* 1925, 560). The method consists in condensing sodium cyanoacetate solution with the appropriate aldehyde when a substituted cyano acrylic acid results. This in turn is converted into the ethyl ester by boiling with absolute alcohol containing 5 per cent dry hydrogen chloride. Addition of hydrogen cyanide to the ester gives a dicyano compound which by boiling with concentrated hydrochloric acid gives the desired succinic acid. The cyano acrylic ester can also be directly prepared by the condensation of the aldehyde with ethyl cyanoacetate in presence of piperidine. (Compare Lapworth and Wikes J. C. S. 1917, 796).

O-hydroxy-phenyl succinic acid has already been prepared by Bredt and Kallen (loc cit.) by adding hydrogen cyanide to coumarin and hydrolysing the resulting cyano compound by sodium hydroxide solution. We now find that acid hydrolysis of the cyano compound gives a cleaner product and in better yield. The m.p. of o-hydroxy-phenyl succinic acid as given by Bredt and Kallen is 150° while we find it to be 172° though no doubt exists as to the identity of our product with that of Bredt and Kallen as our product gave an anhydride and an acetyl anhydride melting at the same temperatures as described by Bredt and Kallen. *O-methoxy phenyl succinic acid* was prepared by (1) methylating o-hydroxy-phenyl succinic acid and (2) by Lapworth's method from o-methoxy benzaldehyde. The use of concentrated hydrochloric acid in the final stage *viz.* the hydrolysis of the dicyano compound, led to partial demethylation which, however, was overcome by using twenty five per cent hydrochloric acid. *M-hydroxy, and M-methoxy-phenyl succinic acids* were prepared by Lapworth's method. P-hydroxy-phenyl succinic acid was prepared by three methods. (1) Lapworth's method from p-hydroxy benzaldehyde. The yield by this method is low (25 per cent) on account of the fact that the aldehyde condensed only partially with sodium cyano acetate solution. (2) By nitration of phenyl succinic acid followed by reduction and diazotisation. Phenyl succinic acid, which can be so conveniently prepared (Organic syntheses Vol. *VIII*, 88) has been already nitrated by Fichter and Walter (Ber. 1909, *42*, 4311) who using nitric acid of density 1·52 obtained a mixture of ortho and para nitro phenyl succinic acids. We find that by using nitric acid of density 1·42 only p-nitro-phenyl succinic acid is obtained. This on reduction with tin and hydrochloric acid gave an excellent yield of *p-amino-phenyl succinic acid.* The diazotisation of the latter, however, gave a large quantity of red colouring matter and only a small yield of p-hydroxy-phenyl succinic acid. (3) By demethylating p-methoxy-phenyl succinic acid of Baker and Lapworth (J. C. S. 1925, 560) by hydrobromic acid. This is the only method to prepare p-hydroxy-phenyl succinic acid in quantity.

All the acids have been characterised by the preparation of the usual derivatives.

EXPERIMENTAL

Sodium cyanoacetate solution was prepared according to the method described in Organic syntheses Vol. *7*, 20. The other steps in the synthesis by Lapworth's method were as given in Organic syntheses Vol. *8*, 88. The compounds are described in tabular form for the sake of brevity.

Name of the compound.	Formula.	Yield and properties.	Found.	Analysis. Required for
Ethyl o-hydroxy phenyl succinate.	$C_{14}H_{18}O_5$	A colourless solid sol in the usual solvents. m. p. 75°.	C, 63.03 H, 6.95	C, 63.16 H, 6.77
Methyl o-hydroxy-phenyl succinate	$C_{12}H_{14}O_5$	Crystallised in needles from alcohol m. p. 98–99°.	C, 60.25 H, 6.11	C, 60.50 H, 5.88
α cyano β o-methoxy-phenyl acrylic acid.	$C_{11}H_9O_3N$.	Yield 36 gms from 24 gms of o-methoxy-benzaldehyde. Crystallised in rectangular plates from water. m. p. 210°.	Eq. Wt. 205.2 N, 7.13	Eq. Wt. 203 N, 6.89
Ethyl α cyano β o-methoxy phenyl acrylate	$C_{13}H_{13}O_3N$.	Obtained either by esterifying the acid or by the condensation of o-methoxy-benzaldehyde with ethylcyanoacetate. fine needles from dilute alcohol. m.p. 75°.	C, 67.21 H, 5.90	C, 67.53 H, 5.63
O-methoxy-phenyl succinic acid	$C_{11}H_{12}O_5$	Yield quantitative. soluble in alcohol, acetic acid and hot water and insoluble in chloroform, benzene and petrol, m. p. 178°.	Eq. Wt. 111.0 C, 58.73 H, 5.50	112.0 C, 58.94 H, 5.36
Methyl-o-methoxy-phenyl succinate	$C_{13}H_{16}O_5$	A colourless liquid b. p. 146° at 17 mm. Density at 32°=1·1155 Refractive Index at 32°=1·5046.	C, 61.64 H, 6.55	C, 61.90 H, 6.35

Ethyl-o-methoxy-phenyl succinate	$C_{15}H_{20}O_5$	Colourless liquid b. p. 165°. at 12 m.m. Density at 32°=1·1111 and Refractive Index at 32°= 1·4938.	C, 64.23 H, 7.50	C, 64.30 H, 7.14
O-methoxy-phenyl succinic anhydride	$C_{11}H_{10}O_4$	Fine needles from benzene. m.p. 130°.	C, 63.84 H, 5.13	C, 64.07 H, 4.86
Mono anilide of o-methoxy-phenyl-succinic acid	$C_{17}H_{17}O_4N$.	Obtained by treating the anhydride with aniline. m.p. 170°.	N, 5.30 Eq. Wt. 302	N, 4.68 Eq. Wt. 299
Mono-p-toluidide of o-methoxy-phenyl-succinic acid	$C_{18}H_{19}O_4N$.	Obtained by treating the anhydride with ptoluidine. m.p. 170°. It depressed the m. p. of mono anilide.	Eq. Wt= 316.5	Eq. Wt. =313
Dianilide of o-methoxy-phenyl succinic acid	$C_{23}H_{22}O_3N_2$	By heating the acid with excess of aniline at 180° for one hour. crystallised from dilute alcohol in needles m.p. 157°.	N, 7.8	N, 7.48
Di-p-toluidide of o-methoxy-phenyl succinic acid	$C_{25}H_{26}O_3N_2$	Similarly prepared crystallised from alcohol m.p. 126°.	N, 7.28	N, 6.97
α cyano β m-hydroxy-phenyl acrylic acid	$C_{10}H_7O_3N$.	quantitative yield crystallised from hot water in colourless needles m.p. 229°.	N, 7.111 Eq. Wt., 191.2	N, 7.40 189
Methyl α cyano β m-hydroxy-phenyl acrylate	$C_{11}H_9O_3N$.	Needles from water or dilute alcohol m. p. 153°.	C, 64.88 H, 4.72	C, 65.02 H, 4.43

Name of the compound.	Formula.	Yield and properties.	Found.	Analysis. Required for
Ethyl α cyano β m-hydroxyphenyl acrylate	$C_{12}H_{11}O_3N$.	Long needles from dilute alcohol m. p. 98°.	C, 66.12 H, 5.25	C, 66.36 H, 5.07
m-hydroxy-phenyl succinic acid	$C_{10}H_{10}O_5$	Soluble in alcohol, water insoluble in benzene and chloroform. Crystallised from ethyl acetate. m.p. 124°.	C, 56.98 H, 5.00	C, 57.14 H, 4.76
Di-anilide of m-hydroxyphenyl succinic acid	$C_{22}H_{20}O_3N_2$	From the acid and aniline at 180°. Crystallised in plates from dilute alcohol. m.p. 145°	N, 8.01	N, 7.78
Di-p-toluidide of m-hydroxyphenyl succinic acid	$C_{24}H_{24}O_3N_2$	Colourless needles m.p. 178°.	N, 7.72	N, 7.21
α cyano β m-methoxyphenyl acrylic acid	$C_{11}H_9O_3N$.	Faintly yellow needles from hot water. m.p. 170.	N, 7.25 Eq. Wt=206	N, 6.89 203
Methyl α cyano β m-methoxyphenyl acrylate	$C_{12}H_{11}O_3N$.	Needles from dilute alcohol m. p. 76°.	N, 6.80	N, 6.45
Ethyl α cyano β m-methoxyphenyl acrylate	$C_{13}H_{13}O_3N$.	Crystallised from ether in needles or plates m. p. 56°.	C, 67.32 H, 5.87	C, 67.53 H, 5.63

m-methoxy-phenyl-succinic acid	$C_{11}H_{12}O_5$	It crystallised from hot water in needles m. p. 176°. It depressed the m. p. of m-hydroxy-phenyl succinic acid.	C, 58.67 H. 5.55 Eq. Wt.=110	C, 58.94 H, 5.36 =112
Methyl m-methoxy-phenyl succinate	$C_{13}H_{16}O_5$	Needles from alcohol m.p. 81°.	C, 61.72 H, 6.48	C, 61.90 H, 6.35
Ethyl m-methoxy-phenyl succinate	$C_{15}H_{20}O_5$	Colourless liquid b.p. 185° at 7 mm.	C, 64.11 H, 7.45	C, 64.30 H, 7.14
m-methoxy-phenyl-succinic anhydride	$C_{11}H_{10}O_4$	Crystallised from chloroform and petrol in prisms. m.p. 57°.	C, 63.82 H, 5.01	C, 64.07 H, 4.86
mono anilide of m-methoxyphenyl succinic acid	$C_{17}H_{17}O_4N$	By treating the anhydride with aniline rectangular plates from dilute alcohol. m. p. 161°.	Equt. Wt. =295	299
mono p-toluidide of m-methoxy-phenyl succinic acid	$C_{18}H_{19}O_4N$	Colourless prisms from dilute alcohol. m. p. 150°.	Eq. Wt.= 314.0	313
Di anilide of m-methoxy-phenyl succinic acid	$C_{23}H_{22}O_3N_2$	By heating the acid with aniline at 180° colourless needles from alcohol m. p. 110°.	N, 7.85	N, 7,48
Di p-toluidide of m-methoxyphenyl succinic acid	$C_{25}H_{26}O_3N_2$	Needles from dilute alcohol m. p. 116°.	N, 7.35	N, 6.97
p-amino-phenyl succinic acid	$C_{10}H_{11}O_4N$.	Obtained by reduction of p nitro-phenyl succinic acid m. p. 226°.	N, 6.93	N, 6.7

Name of the compound.	Formula.	Yield and properties.	Found.	Analysis. Required for
α cyano β p-hydroxy-phenyl acrylic acid	$C_{10}H_7O_3N$.	Prisms from dilute alcohol m. p. 244°.	N. 7.56	N, 7.40
Methyl α cyano β p-hydroxy-phenyl acrylate	$C_{11}H_9O_3N$.	Needles from alcohol m. p. 211°.	C, 65.91 H, 4.71	C, 65.02 H, 4.43
Ethyl α cyano β p-hydroxy phenyl acrylate	$C_{12}H_{11}O_3N$.	Short needles from dilute alcohol.	C, 66.21 H, 5.40	C, 66.35 H, 5.07
p-hydroxy-phenyl succinic acid	$C_{10}H_{10}O_5$	It was soluble in water, alcohol, and hot ethyl acetate. m. p. 164°.	C, 56.83 H, 4.71	C, 57.14 H, 4.76
Methy lp-hydroxy phenyl succinate	$C_{12}H_{14}O_5$	Liquid b. p. 150–160° at 20 mm.	C, 60.28 H, 6.15	C, 60.50 H, 5.88
Di anilide of p-hydroxy-phenyl succinic acid	$C_{22}H_{20}O_3N_2$	Needles from alcohol m. p. 183°.	N, 8.25	N, 7.78

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SYNTHESIS AND DERIVATIVES OF αγ DIPHENYL GLUTACONIC ACID

By

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In connection with the study of the influence of phenyl group in three carbon tautomerism it was considered desirable to have the knowledge of the properties of αγ diphenyl glutaconic acid, the synthesis and derivatives of which, are described in the present communication.

Conrad and Gutzeit (Ann. *222*, 250.) prepared ethyl αγ dicarbethoxy glutaconate by the action of chloroform on ethyl malonate in presence of sodium ethoxide. Using a similar method we have now prepared ethyl αγ diphenyl glutaconate by the action of iodoform on the sodio derivative of ethyl phenyl acetate. The use of chloroform or bromoform in the above reaction was very unsatisfactory. Alkaline hydrolysis of the ester gave αγ diphenyl glutaconic acid which has been characterised by the preparation of such derivatives as methyl ester, anilide, anhydride etc. It may be noted that αγ diphenyl glutaconic acid does not give a hydroxy anhydride.

EXPERIMENTAL

Ethyl αγ diphenyl glutaconate :—Ethyl phenyl acetate (0.2 mol) was added to a cold solution of sodium ethoxide prepared from sodium (7 gms) and absolute alcohol (70 c.c.). Iodoform (40 gms) was then added in small lots. The reaction proceeded with much evolution of heat and separation of sodium iodide. It was left overnight and finally heated on steam bath for one hour. The product obtained by ether extraction after acidification was crystallised from alcohol in needles m.p. 140°. Yield 10 gms. (Found C,74.3 ; H, 6.8 per cent. $C_{21}H_{22}O_4$ requires C, 74.6; H, 6.5 per cent.)

αγ diphenyl glutaconic acid :—The above ester was hydrolysed by boiling with ten per cent sodium hydroxide for four hours when on cooling the sodium salt of αγ diphenyl glutaconic acid separated in needles. It was filtered, dissolved in water, boiled with the addition of animal charcoal filtered and acidified. $\alpha\gamma$ diphenyl glutaconic acid crystallised from dilute alcohol m.p. 230°. (Found C, 72.2 ; H, 5.1 per cent. Equt Wt, 140.3. Ag in the silver salt, 44.1 per cent. $C_{17}H_{14}O_4$ requires C, 72.4 ; H, 5.0 per cent. Equt Wt, 141.0. $C_{17}H_{12}O_4Ag_2$ requires Ag, 43.5 per cent.)

Methyl $\alpha\gamma$ diphenyl glutaconate prepared from the above acid by Fischer Speier method crystallised from methyl alcohol in transparent plates m.p. 169-170°. (Found C, 73.2 ; H, 6.0 per cent $C_{19}H_{18}O_4$ requires C, 73.5 ; H, 5.8 per cent.)

$\alpha\gamma$ diphenyl glutaconic anhydride obtained by treating the acid with excess of acetyl chloride on water bath for two hours crystallised from benzene and petrol in fan like needles m.p. 120°. It was insoluble in a cold solution of sodium carbonate. (Found C, 77.1 ; H, 4.8 per cent. $C_{17}H_{12}O_3$ requires C, 77.3 ; H, 4.6 per cent.)

Dianilide of $\alpha\gamma$ diphenyl glutaconic acid prepared by heating the acid with excess of aniline at 200° for half an hour crystallised from benzene in needles m.p. 234°. (Found N, 7.0 per cent. $C_{29}H_{24}O_2N_2$ requires N, 6.5 per cent.)

Reduction of $\alpha\gamma$ diphenyl glutaconic acid by sodium amalgam gave an acid crystallising from water in feather like needles m.p. 189-190° Equt Wt, 143.0. L. Souther (J. A. C. S. 1924, *46*, 1301) gives the m.p. of $\alpha\gamma$ diphenyl glutaric acid as 185°

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CHALKONES: REACTIVITY OF SOME CHALKONE OXIDES.

By

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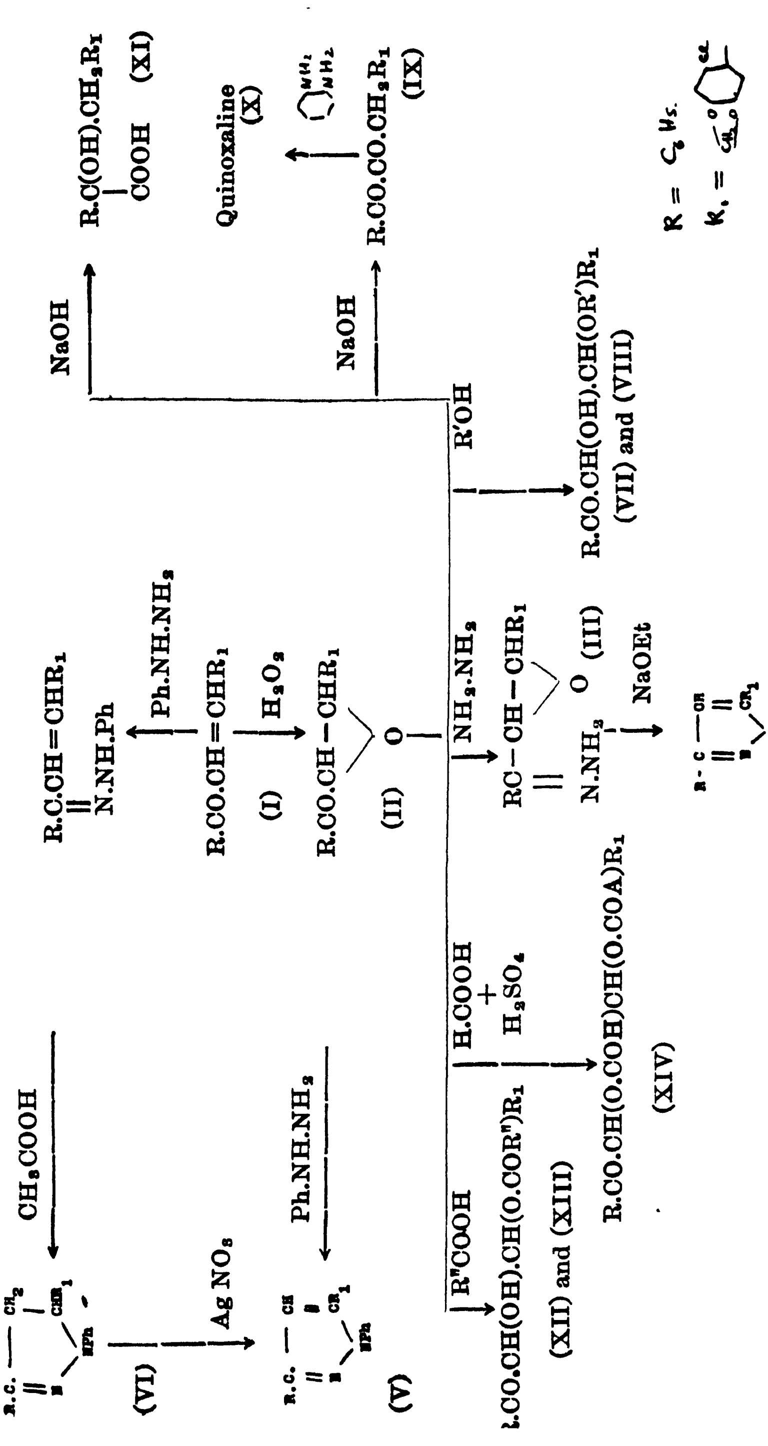
Baker and Robinson (J. C. S., 1932, 1798) claimed that the reactions involved in passing from the chalkone oxide $\mathrm{R.CO.}\underset{\mathrm{O}}{\underbrace{\mathrm{CH.CH}}}\mathrm{.R_1}$ through the glycollic acid $\mathrm{RC(OH)\ (COOH)CH_2R_1}$ to the desoxybenzoin $\mathrm{R.CO.CH_2R_1}$ gave in general, almost quantitative yields at each stage. Dodwadmath and Wheeler (Proc. Indian Acad. Sciences, 1935, *2*, 438) found that, while the reactions proceeded with the oxide of phenyl 3:4-methylenedioxystyryl ketone, the presence of a nitro-group in the 6-position in the methylenedioxystyryl nucleus made it impossible to prepare the glycollic acid. It has now been found that the presence of a chlorine atom in the 6-position though it does not inhibit the reaction completely, greatly reduces the yield of the glycollic acid. Experiments with the oxides of the corresponding bromo-chalkone and of 2-methoxy-1-naphthyl 6-bromo-3:4-methylenedioxystyryl ketone gave similar results. This method, first developed by Widman (Ber., 1916, *49*, 477) for the synthesis of desoxybenzoins from oxides, appears, therefore, to be limited in its application.

Phenyl 6-chloro-3: 4 methylenedioxystyryl ketone (I) yielded the corresponding *oxide* (II) by the method of Weitz and Scheffer (Ber., 1921, *54*, 2327). (II) with alcoholic hydrazine hydrate gave a *hydrazone* (III); (III) is taken to be a hydrazone and not a hydroxydihydropyrazole, because it does not form a nitroso-derivative. (Cf., Widman, Ber., 1916, *49*, 2781). With sodium ethoxide (III) yielded *3-phenyl-5-(6'-chloro-3':4'-methylenedioxyphenyl) pyrazole* (IV). (II) on treatment with phenylhydrazine in acetic acid solution gave directly *1:3-diphenyl-5-(6'-chloro-3':4'-methylenedioxyphenyl) pyrazole* (V). (I) with phenylhydrazine in acetic acid yielded a phynylhydrozone; the presence of a dihydropyrazole was excluded by the fact that the product did not give Knorr's pyrazoline reaction: *i.e.* a trace dissolved in sulphuric acid gave no blue colour with a drop of ferric chloride solution. (Cf., Auwers and Voss, Ber., 1909, *42*, 4417); after being boiled with acetic acid the hydrazone gave a product which answered Knorr's test and was the *dihydropyrazole* (VI); this when heated with aqueous alcoholic silver nitrate was readily oxidised to (V).

When a suspension of (II) in methyl alcohol was treated with sulphuric acid, the oxide ring opened with production of *phenyl α-hydroxy-β-methoxy-β-(6-chloro-3:4-methylenedioxyphenyl) ethyl ketone* (VII); ethyl alcohol reacted similarly to give *phenyl α-hydroxy-β-ethoxy-β-(6-chloro-3:4-methylenedioxyphenyl) ethyl ketone* (VIII); the position of the alkoxy-groups in (VII) and (VIII) is established by the results of Robinson and Baker *(loc. cit.)* and Dodwadmath and Wheeler *(loc. cit.)*, who found that similar alkoxy-compounds gave α-diketones when boiled with alkali. When (II) was boiled with alcoholic sodium hydroxide for one minute it yielded *phenyl 6-chloro-3:4-methylenedioxybenzyl diketone* (IX) the constitution of which as an α-diketone was fixed by the fact that with *o*-phenylenediamine it gave 2-phenyl-3-(6'-chloro-3':4'-methylenedioxybenzyl) quinoxaline (X), Prolonged treatment of the oxide with alkali gave a poor yield of *phenyl (6-chloro 3:4-methylenedioxybenzyl) glycollic acid* (XI); sufficient was not obtained to permit of the preparation of the corresponding desoxybenzoin from the acid.

Direct treatment of (II) with formic and acetic acids yielded respectively *phenyl α-hydroxy-β-formoxy-β-(6-chloro-3:4 methylenedioxyphenyl) ethyl ketone* (XII) and *phenyl α—hydroxy β-acetoxy β-(6-chloro-3: 4 methylenedioxyphenyl) ethyl ketone* (XIII). A mixture of formic and sulphuric acid gave *phenyl α,β-diformoxy-β-(6-chloro-3:4-methylenedioxyphenyl) ethyl ketone (XIV).*

A number of analogous compounds from phenyl 6-bromo-3:4-methylenedioxystyryl ketone were also prepared; the yields were in all instances similar. Some of the reactions were carried out with 1-methoxy-2-naphthyl 6-bromo-3:4-methylenedioxystyryl ketone, as keto-ethylene oxides of the naphthalene series do not appear hitherto to have been examined; here also no satisfactory yield of the glycollic acid could be obtained.


R.CO.CH=CHR₁ (I)
Ph.NH.NH₂
R.C.CH=CHR₁ ‖ N.NH.Ph
H₂O₂
R.CO.CH—CHR₁ O (II)
NH₂.NH₂
RC—CH—CHR₁ ‖ N.NH₂ O (III)
NaOEt
(IV)
R'OH
R.CO.CH(OH).CH(OR')R₁ (VII) and (VIII)
NaOH
R.CO.CO.CH₂R₁ (IX)
Quinoxaline (X)
NH₂ NH₂
NaOH
R.C(OH).CH₂R₁ COOH (XI)
R"COOH
.CO.CH(OH).CH(O.COR")R₁ (XII) and (XIII)
H.COOH + H₂SO₄
R.CO.CH(O.COH)CH(O.COA)R₁ (XIV)
CH₃COOH
(VI)
Ag NO₃
Ph.NH.NH₂
(V)
R = C₆H₅.
R₁ =

EXPERIMENTAL

COMPOUNDS FROM PHENYL 6-CHLORO-3.4-METHYLENEDIOXYSTYRYL KETONE

Phenyl 6-chloro-3:4-methylenedioxystyryl ketone (I): A hot alcoholic solution of 6-chloro piperonal (19 g.) and acetophenone (12 g) was treated with aqueous sodium hydroxide solution (50 c.c. 10%); the *precipitate* (24.5 g.) formed after 30 minutes had m.p. 136° on crystallisation from alcohol. (Found: Cl, 11-8, $C_{16}H_{11}O_3Cl$ requires Cl, 12.4%)

Oxide of phenyl 6-chloro-3:4-methylenedioxystyryl ketone (II): A thin paste of (I; 10 g.) and alcoholic acetone (80 c.c. 1:1) was treated with perhydrol (20 c.c.) and sodium hydroxide solution (4 c.c.; 4N), and the mixture was kept at room temperature until solution of the chalkone and separation of the oxide had ceased. Addition of water completed the precipitation. The *product* (7.5 g.) after crystallisation from acetone had m.p. 103-104° (Found: Cl, 11.6, $C_{16}H_{11}O_4Cl$ requires Cl, 11.7%). *The hydrazone* (III) (1.5 g.) m.p. 179°, separated on cooling an alcoholic solution of (II; 2 g.) and hydrazine hydrate (2 c.c.) which had been boiled for 5 minutes. The *product* was recrystallised from alcohol. (Found: Cl, 11.2, $C_{16}H_{13}O_3N_2Cl$ requires Cl, 11.2%). It did not yield a nitrosoderivative with KNO_2 in acetic acid and was therefore a hydrazone and not a hydroxydihydropyrazole (Cf., Widman, *loc. cit.*, p. 2781).

3-Phenyl-5-(6'-chloro-3':4'-methylenedioxyphenyl) pyrazole (0.6 g.) (IV) separated in yellowish crystals from an alcoholic solution of (III; 1 g.) and sodium ethoxide (0.5 g. Na) which had been boiled for about 5 minutes. The *product* after recrystallisation from alcohol had m.p. 171° (Found: Cl, 11.7. $C_{16}H_{11}O_2N_2Cl$ requires Cl, 11.9%)

1:3-Diphenyl-5-(6'-chloro-3':4'-methylenedioxyphenyl) pyrazole (V) separated from a solution of (II; 1 g.) and phenylhydrazine (0.4 g.) in acetic acid, which had been heated at 100°, cooled and poured into dilute hydrochloric acid. The *product* (0.7 g.) separated from alcohol in crystals having m.p. 149-150° (Found: C, 69.8; H, 4.5., $C_{22}H_{15}O_2N_2Cl$ requires C, 70.4; H, 4.0%).

1:3-Diphenyl-5-(6'-chloro-3':4'-methylenedioxyphenyl)-4:5-dihydropyrazole (VI). A solution of (I; 2.5 g.) and phenylhydrazine (4.5 c.c.) in acetic acid was warmed for about five minutes and then treated with dilute hydrochloric acid. The resulting precipitate gave no blue coloration with sulphuric acid and a drop of ferric chloride solution, and was, therefore, a phenylhydrazone and not a dihydropyrazole. It was boiled with acetic acid; on dilution after cooling the *precipitate* answered Knorr's test and after recrystallisation from alcohol had m.p. 156° (Found: C, 70.0; H, 4.5. $C_{22}H_{17}O_2N_2Cl$, requires C, 70.1; H, 4.5%). It was boiled with aqueous alcoholic silver nitrate and the precipitate obtained after the dilution of the filtrate with water was recrystallised from alcohol. It then had m.p. 149° not depressed by (V) prepared from the oxide as described above.

Phenyl-α-hydroxy-β-methoxy-β-(6-chloro-3:4-methylenedioxyphenyl) ethyl ketone (VII). A suspension of (II; 1 g.) in methyl alcohol (25 c.c.) was treated with a mixture of sulphuric acid and methyl alcohol (5 c.c. 4:1), and the resulting solution boiled for a few minutes and cooled; the precipitate thus obtained (0.6 g.) had m.p. 169° after recyrstallisation from methyl alcohol. (Found: Cl, 10.2., $C_{17}H_{15}O_6Cl$ requires Cl, 10.6%).

phenyl-α-hydroxy-β-ethoxy-β-(6-chloro-3:4-methylenedioxyphenyl) ethyl ketone (VIII) was similarly prepared using ethyl alcohol: it had m. p. 134–138° after recrystallisation from ethyl alcohol (Found; Cl, 10.2., $C_{18}H_{17}O_5Cl$ requires Cl, 10.2%).

Phenyl 6-chloro-3:4 methylenedioxybenzyl diketone (IX) separated as a paste from an alcoholic solution of (II; 1 g.) which had been treated with sodium hydroxide (0.5 g.) in alcohol (10 c. c.) boiled for 1 minute, and acidified with dilute hydrochloric acid. After crystallisation from alcohol, it formed yellow needles (0.8 g.) having m. p. 157–158°. It gave a reddish colour with alcoholic ferric chloride (Found: Cl, 11.5., $C_{16}H_{11}O_4Cl$, requires Cl, 11.7%)

2-Phenyl-3-(6'-chloro-3': 4'-methylenedioxybenzyl) quinoxaline (X) separated on cooling a solution of (IX; 0.2 g.) and *o*-phenylenediamine (0.1 g.) in alcohol, which had been boiled for five minutes; after recrystallisation from alcohol it had m. p. 114° (Found: Cl, 9.5., $C_{22}H_{15}O_2N_2Cl$ requires Cl, 9.5%)

Phenyl-(6 chloro-3: 4-methylenedioxybenzyl) glycollic acid (XI): An alcoholic solution of (II; 1 g.) and sodium hydroxide (0.5) in alcohol (10 c. c.) which had been heated under reflux for four hours was acidified with dilute hydrochloric acid; the pasty precipitate (0.2 g.) separated from alcohol in yellow crystals having m. p. 157°. (Found: Cl, 11.0., $C_{16}H_{13}O_5Cl$ requires Cl, 11.1%).

Phenyl α-hydroxy-β-formoxy-β-(6-chloro-3:4-methylenedioxyphenyl) ethyl ketone (XII) precipitated as a paste from a solution of (II; 1 g.) in formic acid (7 c. c.) which had been heated to 100°, cooled and diluted with water. The product (0.3 g.) separated from alcohol in crystals having m. p. 170°. (Found: Cl, 10.2. $C_{17}H_{13}O_{6}$ Cl requires Cl, 10.2%).

Phenyl α-hydroxy-β-acetoxy-β-(6-chloro-3:4-methylenedioxyphenyl) ethyl ketone (XIII) separated from a solution of (II; 1 g.) in acetic acid (8 c. c.) which had been warmed at 100° for a minute, and diluted with water after 2 hours. It separated from alcohol in crystals (0.5 g.) having m. p. 155–156°. (Found: Cl, 9.9 $C_{18}H_{15}O_{6}Cl$ requires Cl. 9.8%).

Phenyl α β-diformoxy-β-(6-chloro-3:4-methylenedioxyphenyl) ethyl ketone (XIV) separated as a paste from a solution of (II; 1 g.) in formic acid (7 c. c.) which had been treated with a mixture of formic acid and sulphuric acid (2 c. c.; 4:1), heated at 100° for 1 minute, kept for two hours, and diluted with water. It separated from acetic acid in crystals (0.3 g.) having m. p. 145-146° (Found: Cl, 9.4, $C_{18}H_{13}O_{7}Cl$ requires Cl, 9.4%).

COMPOUNDS FROM PHENYL 6-BROMO-3: 4-METHYLENEDIOXYSTYRYL KETONE.

Phenyl 6-bromo-3: 4-methylenedioxystyryl ketone (Dodwadmath and Wheeler, *loc. cit.*) yielded in the same way the following series of compounds:—*Oxide of phenyl 6-bromo-3: 4-methylenedioxystyryl ketone* (Found: Br., 22.8, $C_{16}H_{11}O_{4}$ Br requires Br., 23.0%) m. p. 99-100°; *hydrazone of oxide* (Found: Br., 22.7, $C_{16}H_{13}O_{3}N_{2}$ Br requires Br., 22.2%) m. p. 182-183°; 3-*phenyl-5-(6'-bromo-3': 4'-methylenedioxy-phenyl) pyrazole* (Found: Br, 23.6. $C_{16}H_{11}O_{2}N_{2}$ Br requires Br, 23.3%) m. p. 158-159°; *1:3-diphenyl-5 (6'-bromo-3':4'-methylenedioxyphenyl) pyrazole* (Found: Br., 19.3, $C_{22}H_{15}O_{2}N_{2}$ Br requires Br., 19.1%), m. p. 149-150°; *1 : 3-diphenyl-5-(6'-bromo-3': 4'-methylenedioxyphenyl) 4 : 5-dihydropyrazole* (Found: Br. 18.8, $C_{22}H_{17}O_{2}N_{2}$ Br requires Br., 19.%) m. p. 165-167°; *phenylα-hydroxy-β-methoxy-β-(6-bromo-3:4 methylenedioxyphenyl) ethyl ketone* (Found: Br., 21.3, $C_{17}H_{15}O_{5}$ Br. requires Br. 21.1%), m. p. 165°; *phenyl α-hydroxy-β-ethoxy-β-(6-bromo-3:4-methylenedioxyphenyl) ethyl ketone* (Found: C, 55.6. H. 4.2., $C_{18}H_{17}O_{5}$ Br requires C, 55. O; H, 4.3%) m. p. 100°; *phenyl 6-bromo-3-4-methylenedioxybenzyl diketone* (Found: Br. 23.6, $C_{16}H_{11}O_{4}$ Br requires Br. 23.1%) m. p. 151°, and *phenyl-(6-bromo-3:4-methylenedioxybenzyl) glycollic acid* (Found : Br, 22.2, $C_{16}H_{1}O_{5}$ Br, requires Br, 21.9%), m. p. 154°,

COMPOUNDS FROM 1-METHOXY-2-NAPHTHYL 6-BROMO-3: 4-METHYLENEDIOXYSTYRYL KETONE.

1-Methoxy-2-naphthyl 6-bromo-3:4-methylenedioxystyryl ketone:—A hot alcoholic solution of 6-bromopiperonal (25 g.) and 2-acetyl-1-methoxynaphthalene (20 g.) was treated with aqueous sodium hydroxide (50 c. c. ; 10%); the *precipitate* (32 g) formed after 30 minutes had m. p. 147° C on crystallisation from alcohol. (Deshmukh; private communication).

Oxide of 1-methoxy-2-naphthyl 6-bromo-3:4-methylenedioxystyryl ketone: A thin paste of the chalkone (10 g.) and alcoholic acetone (80 c.c. 1:1) was treated with perhydrol (20 c.c.) and sodium hydroxide solution (4 c.c., 4N), and the mixture was kept at room temperature until solution of the chalkone and separation of the oxide had ceased. Addition of water completed the precipitation. The *product* (6 g.) after crystallisation from acetone had m. p. 158°, (Found, C, 58.9; H, 3.6, $C_{21}H_{15}O_5$ Br requires C, 59.0; H, 3 5%. *The hydrazone* (0.9 g.) separated on cooling an alcoholic Solution of the oxide (2 g.) and hydrazine hydrate (2 c.c.) which had been boiled for five minutes. The product after recrystallisation from alcohol had m. p. 185° (Found: Br, 18 5, $C_{21}H_{17}O_4N_2$ Br) requires Br, 18.1%). It did not yield a nitroso derivative with KNO_2 in acetic acid and was therefore a hydrazone and not a hydroxydihydropyrazole. (Cf., Widman, *loc. cit.*).

1-methoxy-2-naphthyl α-hydroxy-β-ethoxy-β-(6-bromo-3:4-methylenedioxyphenyl) ethyl ketone was similarly prepared using ethyl alcohol. It had m. p. 181-182° after recrystallisation from ethyl alcohol. (Found: Br, 16.8, $C_{23}H_{21}O_6$ Br requires Br, 16.9%)

1-Methoxy-2-naphthyl 6-bromo-3:4-methylenedioxybenzyl diketone separated as a sticky mass from an alcoholic solution of the oxide (1 g,) which had been treated with sodium hydroxide (0.5g.) in alcohol (10 c.c.), boiled for a minute and acidified with dilute hydrochloric acid. After crystallisation from alcohol it gave yellow crystals (0.8 g.) having m. p. 164-165°. (Found: Br, 18.8, $C_{21}H_{15}O_5$ Br requires Br, 18.7%).

2(1-methoxy-2'-naphthyl)-3-(6'-bromo-3':4'-methylenedioxybenzyl)-quinoxaline separated in light yellow crystals on cooling a solution of the preceding diketone (0.4 g.) and *o*-phenylenediamine (0.2 g.) in alcohol, which had been boiled for five minutes; after recrystallisation from alcohol it had m. p. 203°. (Found: Br, 15.8 $C_{27}H_{19}O_3N_2$ Br requires Br, 16.0%).

1-Methoxy-2-naphthyl α-hydroxy-β-formoxy-β-(6-bromo-3: 4-methylenedioxyphenyl) ethyl ketone separated as a paste from a solution of the oxide (1 g.) in formic acid (7 c. c.) which had been kept for an hour and diluted with water. The *product* (0.2 g.) separated from alcohol in crystals having m. p. 158-159°. (Found: Br, 17.2 $C_{22}H_{17}O_7Br$ requires Br, 16.9%).

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A MODIFIED METHOD FOR THE CONVERSION OF COUMARIN DERIVATIVES INTO O-METHXOY- CINNAMIC ACIDS.

By

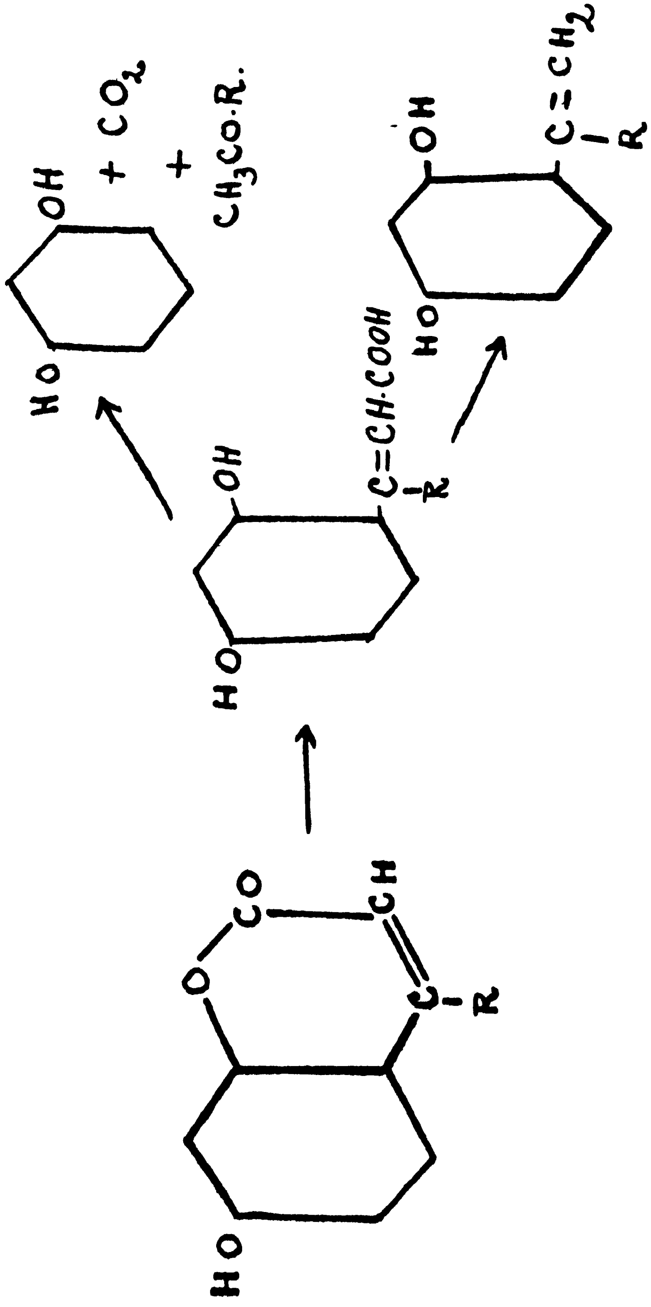
N. M. SHAH AND R. C. SHAH

Much of the confusion in the earlier work on coumarins and chromones arose because of a want of a satisfactory method of distinguishing them. Earlier workers mainly depended upon the hydrolytic products obtained through alkaline reagents, which often led to erroneous conclusion.

The initial action of alkali is to open the lactone ring of the coumarin with the formation of a salt of a coumarinic acid, which on acidification will regenerate the original coumarin. If, after hydrolysis, the closure of the coumarin ring is prevented by subsequent methylation of the hydroxyl group, it will generally give a methoxy-cinnamic acid derivative. This forms the basis of Canter and Robertsons' method which is the only positive diagnostic test for coumarin structure. They used this method to conclusively prove that the product of the condensation of resorcinol with methyl-a-methyl acetoacetate in presence of phosphoric anhydride (Simonis reaction) was a coumarin derivative by converting it into an o-methoxy-cinnamic acid (J. 1931, 1875). This is a more trustworthy method of determining the presence of coumarin structure than the method depending upon alkaline hydrolysis. The conversion is carried out (1) by heating the substance with alkali for sometime whereby the lactone ring opens and (2) subsequently methylating the hydroxyl group by addition of dimethyl sulphate to prevent the ring formation.

Canter and Robertsons' elegant method though widely used, does not succeed in all cases. It is possible that in the first stage, the action of alkali may go further, leading to complications as shown below:—

(Wittenberg, J. Pr. Chem, 1880, *21*, 26; Pechmann and Cohen, Ber, 1884, *17*, 2129, 2137; Limaye, Ber. 1934, *67*, 12)


HO
O
CO
CH
C—R
HO
OH
C=CH·COOH
R
HO
OH
+ CO$_2$
+
CH$_3$CO·R.
HO
OH
C=CH$_2$
R

In connection with the work on coumarins in which the authors are engaged for some time past, the Robertson method was applied in several cases, in some of which it failed. It was then thought that the failure may perhaps be due to the action of alkali on the o-hydroxy-cinnamic acid formed and that if the-OH group was methylated *immediately* it was formed, the chances of the above complications taking place may be lessened. Trial experiments were made in which, to the coumarin dissolved in acetone, dimethyl sulphate was first added, followed by alkali solution (20%KOH) and alternate additions of more quantities of the methyl sulphate and alkali as required. As trial experiments gave promising results, the method was tried in a number of cases successfully.

The typical procedure followed is described in case of 4-methyl-coumarin as under:—

4-methylcoumarin (1 g.) was dissolved in a least quantity of acetone and dimethyl sulphate (10 c.c.) added. To this mixture, KOH (20%; 25 c.c.) was added, the mixture well shaken and heated on boiling water-bath. More quantity of KOH solution and dimethyl sulphate (in all, 15 c.c.) were alternately added and heating continued for an hour, keeping the mixture alkaline throughout. It was cooled, acidified and extracted with ether. The ethereal extract was treated with sodium bicarbonate solution (5%). The aqueous layer was separated and acidified when a white ppt. was obtained. It was collected and crystallised from a mixture of benzene and petroleum ether, m.p. 123-124°.

It appears from the results obtained that this method is more satisfactory than the Robertson method. The cinnamic acids are easily obtained in a state of purity in satisfactory yields. In some cases where the Robertson method fails, the modified method has given the cinnamic acids satisfactorily, *e. g.* in case of (1) 7: 8-dihydroxy-4- methylcoumarin- 3- propionic acid, (Shah and Shah, Ber, 1938, *71*, 2079). (2) 5-hydroxy 8-ethyl-4-methyl coumarin (Sethna and Shah, J. 1938, 1068) and (3) 7 hydroxy-3—(ββββ-trichloro-a-hydroxy-ethyl)-4-methyl coumarin (Unpublished).

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SIMPLIFIED METHODS FOR THE PREPARATION OF ARYLAMIDES OF O-TOLUIC, O-CHLOROBENZOIC AND O-METHOXYBENZOIC ACIDS.

By

LATE N. W. HIRWE, G. V. JADHAV AND D. R. SUKHTANKAR.

Generally arylamides are conveniently prepared by the Schotten-Baumann reaction, but when pure acid chlorides cannot be easily obtained as in the case of salicylic acid, the use of a mixture of an acid, an amine and phosphorus trichloride has been suggested by Wanstrat (Ber., 1873, *6*, 337).

Arylamides of O-toluic, O-chlorobenzoic and O-methoxybenzoic acids were required in connection with work on the interaction of sulphuryl chloride with arylamides of aromatic acids described separately. Examination of the literature showed that such known amides were often prepared by indirect processes, *e.g.* o-toluanilide was prepared from anti-phenyl-o-tolyl ketoxime by Smith (Ber., 1891, *24*, 4047) and o-tolu-p-toluidide from o-tolyl-p-tolyl ketoxime by Scharwin and Schorigin (Ber., 1903, *36*, 2027) by the Beckmann change, others were either unknown or prepared by similar indirect methods.

The application of Wanstrat's methods gave satisfactory results with arylamides of o-toluic and o-chlorobenzoic acids.

With o-methoxybenzoic acid the use of thionyl chloride, acid and amine worked out satisfactorily.

EXPERIMENTAL

The acid (3 mol.), amine (3 mol.) and phosphorus trichloride (1 mol.) were heated at 120° for about four hours unless otherwise mentioned. The product was washed with hydrochloric acid, with alkali and finally with water and then crystallised from a suitable solvent.

o-toluanilide Crystallised from glacial acetic acid in needles, m. p. 128°. Yield, 75%. Smith (loc. cit.) gives m.p. 125°.

o-*tolu*-o-*toluidide*—Soluble in benzene, alcohol, glacial acetic acid and crystallised from the last solvent in needles, m.p. 140°. Yield, 80%. Found: N.5.9, $C_{15}H_{15}ON$ requires N,6.2 per cent.

o-*tolu*-m-*toluidide*—Solubility as in the case of ortho isomer and crystallised in needles, m.p.144°. Yield, 80%. Found. N,6.2, $C_{15}H_{15}ON$ requires 6.2 per cent.

o-*tolu*-p-*toluidide*—Crystallised from glacial acetic acid in needles, m.p. 142°. Scharwin and Schorigin (loc.cit.) gave m.p.144°

o-*totu*-p-*chloranilide*—Heated for half an hour only. Crystallised from alcohol in needles, m.p. 133°. Found: Cl, 14.2, $C_{14}H_{12}ONCl$ requires Cl, 14. 5 per·cent.

o-*chlorobenz*-o-*chloranilide*—Soluble in benzene, alcohol, acetic acid and crystallised from acetic acid in needles, m. p. 100°. Found: Cl,26.9,$C_{13}H_{9}$,$ONCl_{2}$ requires Cl,26.7per cent.

o-*chlorbenz*-m-*chloranilide*—Soluble in the same solvents as ortho isomer and crystallised from acetic acid in needles, m.p. 129-130°. Found: Cl,26.4, $C_{13}H_{9}ONCl_{2}$ requires Cl,26.7 per cent.

o-*chlorbenz*-p-*chloranilide*—Resembles the isomers in solubility and crystalline form, m.p.121°. Found: Cl, 26.3,$C_{13}H_{9}ONCl_{2}$ requires Cl,26.7 per cent.

o-*methoxybenzanilide*—O-methoxybenzoic acid (20 gm.) and thionyl chloride (25 gm.) were boiled under reflux for about three hours and the reaction mixture was then added to aniline (10 gm.) dissolved in dry benzene and shaken for some time. The semi-solid separated after removal of benzene was thoroughly washed and then crystallised from acetic acid in needles, m.p.69°. Found: N,6.2, $C_{14}H_{13}O_{2}N$ requires N,6.2, per cent.

Haller. (C.r.1895,*121*,189,) prepared it from o-methoxybenzoic acid and phenylisocyanate and gave m.p.62°,

o-*methoxybenz*-o-*anisidide*—It was prepared in the same way as anilide but in this case a solid separated after removal of benzene. It was first washed with dilute hydrochloric acid, then with alkali and finally with water. The substance was soluble in benzene, alcohol and acetic acid. It was crystallised from acetic acid in needles, m. p. 100°. Found : N,5.1,$C_{15}H_{15}O_{3}N$ requires N,5.5 per cent.

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CLIMATOLOGY OF BOMBAY

By

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INTRODUCTION

The climate of a locality is in its general features determined by its geographical situation and the distribution of land, sea and mountains in the area surrounding it. Bombay being a sea-level station at the latitude of 19°N and being almost surrounded by water, has on the whole a warm, moist climate, but its situation on the west coast of India with the great Asiatic continent to its north, and the Arabian Sea and the Indian Ocean to its west and south, causes important seasonal changes in its climate. In order to appreciate the annual variation of the climatic features of Bombay, one has to consider it as part of a general large-scale variation which takes place over the major part of India and its neighbourhood. With the annual movement of the sun from south to north and back, there is a seasonal variation in the nature of the air which flows over the country. During the months December to April, the air flowing over Bombay has been for long over land, and is hence comparatively dry, except for a thin layer near the ground. There is in this season practically no rain and little cloud and there is appreciable night cooling. On the other hand, in the months June to September, the air stream that flows over Bombay has had a long travel over sea and is hence charged with moisture to a depth of 2 to 4 miles. 94 per cent of the annual rainfall occurs in these months and there is only a very small diurnal variation of temperature. The proximity of the Western Ghats which rises to a height of 2000 to 3000 ft. within a distance of 40 miles to the east of Bombay causes increased rainfall during the monsoon and accentuates the daily land and sea-breezes in the non-rainy months.

AIR-MOVEMENT OVER BOMBAY

The state of the air near the ground as regards temperature and moisture content is a function of its recent history. In order therefore to understand the variations of these properties, it is of importance to know the sources of air at different times.

TABLE 1

MEAN MONTHLY WIND DIRECTION AND SPEED

(in miles per hour) at Bombay.

(Height: 100 ft. above mean sea-level)

Month		Hour (local time)							
		0-1	3-4	6-7	9-10	12-13	15-16	18-19	21-22
January	Dir.	NNE	NNE	NE	NE	NW	NW	NW	NNW
	Vel.	4.7	5.4	6.2	6.3	6.5	9.8	10.1	6.3
February	Dir.	N	N	NE	NE	NW	NW	NW	NNW
	Vel.	5.1	5.6	5.6	5.8	8.1	11.2	10.5	6.4
March ...	Dir.	NW	NNW	NNE	N	WNW	WNW	NW	NW
	Vel.	6.2	5.4	4.9	5.7	9.6	12.1	9.8	6.1
April ...	Dir.	NW	NNW	NNE	WNW	WNW	WNW	WNW	NW
	Vel.	6.2	4.8	4.2	5.6	9.8	12.3	9.6	6.5
May ...	Dir.	W	W	W	W	W	W	W	W
	Vel.	6.0	5.2	4.6	6.2	9.0	10.8	8.6	6.5
June ...	Dir.	SW	SW	SW	SW	WSW	WSW	WSW	SW
	Vel.	10.0	9.8	9.5	9.9	10.8	11.7	10.5	10.1
July ...	Dir.	WSW	WSW	WSW	WSW	WSW	WSW	WSW	WSW
	Vel.	12.2	12.6	12.3	12.0	12.4	12.8	12.2	11.7
August...	Dir.	WSW	WSW	WSW	WSW	WSW	WSW	WSW	WSW
	Vel.	10.4	10.8	10.5	10.3	11.1	11.5	10.5	9.8
September	Dir.	W	W	WSW	WSW	W	W	WNW	W
	Vel.	6.5	6.6	6.6	6.8	8.2	9.5	7.9	6.4
October	Dir.	NNE	NE	ENE	ENE	WNW	WNW	NW	N
	Vel.	5.0	5.3	5.7	5.6	6.5	9.2	8.0	5.3
November	Dir.	NE	ENE	ENE	ENE	NNW	NW	NNW	N
	Vel.	4.6	6.0	7.2	6.6	5.4	8.6	9.1	5.4
December	Dir.	NE	NE	ENE	ENE	NNW	NW	NNW	N
	Vel.	4.5	5.9	7.2	6.9	5.2	8.4	9.6	5.8

In table 1 are given the mean monthly directions and speeds of wind measured at the Colaba Observatory, Bombay, with the anemometer at a height of 100 ft. of above mean sea-level. The mean values of wind direction and speed are given for eight hourly intervals distributed throughout the day. It will be seen that during the months May to September the mean wind directions vary from west to south-west, there being little diurnal variation. In the rest of the year, there are two prominent wind directions, one from north-west and the other from north-east. In general, the north-easterlies which are from land occur during the forenoon hours and the north-westerlies from sea in the afternoons. There is a seasonal variation in the duration of these land and sea-breezes, the land breezes prevailing during all the forenoon hours in November, blowing only for two or three hours in the morning in April, and dying out in May. A good picture of the mean surface airflow over Bombay is given by the trajectories of an imaginary balloon floating in air and being carried by the wind from one midnight to the next (Fig. 1).

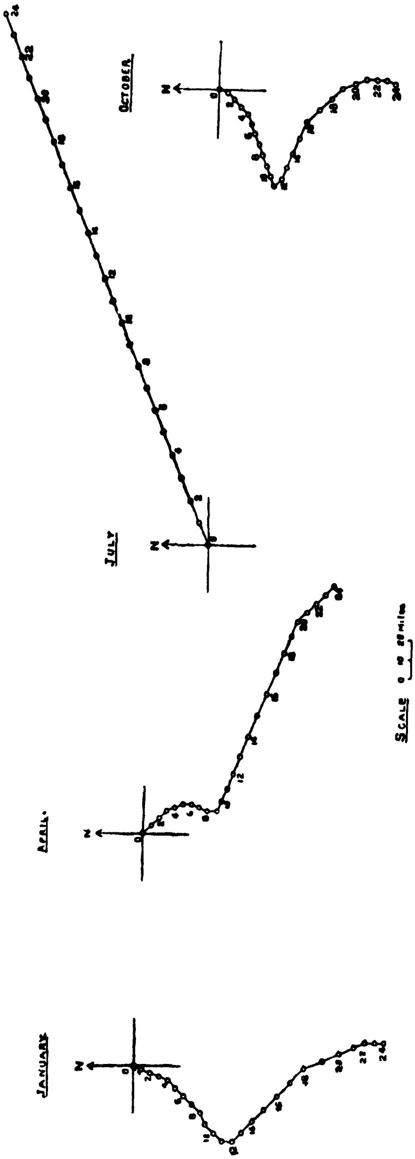

Fig. Trajectories of mean air movement at about 100 ft. above ground over Bombay.

The trajectories make it clear that in the non-rainy months, while the late night and morning winds tend to carry the air of the mill areas of north Bombay to Malabar Hill and its south, this air would be swept off towards the coastal hills by the afternoon sea-breeze and be replaced by fresh air from the sea. There is thus a daily dissipation of polluted air by the agency of the sea-breeze.

For the sake of completeness, I have added in Table 2, the mean monthly wind directions and speeds over Bombay at different heights above sea-level measured by means of pilot balloons. The data refer to the year 1936.

TABLE 2

COLABA (BOMBAY)

Monthly mean directions and speeds of upper winds 1936.

Height in km.	0.5 km.		1.0 km.		2.0 km.		3.0 km.		4.0 km.		6.0 km,	
	D	V	D	V	D	V	D	V	D	V	D	V
		m. p. h.		m. p. h.		m. p. h.		m. p. h.		m. p. h.		m. p. h.
January ...	NNE	13	N	10	SSW	15	WSW	18	W	25	W	39
February ...	N	12	N	11	SSW	12	SW	15	W	21	W	41
March ...	NE	14	NE	13	WSW	11	SSW	13	WSW	14	WSW	26
April ...	N	11	NNW	14	NW	16	SW	13	SW	17	WNW	22
May ...	WSW	10	NW	13	NW	15	SW	9	SSE	13	N	11
June ...	WSW	19	WSW	20	W	17	W	13	WSW	9	SSW	10
July ...	WSW	25	WSW	26	WSW	23	WSW	16	...	...	...	...
August ...	W	23	W	23	WSW	18	WNW	9	...	...	...	...
September ...	W	15	W	15	S	15	NE	11	NE	8	E	9
October ...	ENE	15	ENE	16	NE	14	ENE	11	NNE	13	N	14
November ...	E	17	ESE	14	ESE	11	E	12	E	13	W	17
December ...	ENE	16	E	15	SSW	12	NW	13	NW	18	WNW	30

TEMPERATURES AND HUMIDITIES

The monthly mean, maximum and minimum temperatures of Bombay and the mean values of relative humidity and vapour pressure are given in Table 3. The number of hours of bright sunshine (per day) in each month is also added.

TABLE 3—SUNSHINE, TEMPERATURE AND HUMIDITY AT BOMBAY

Month	Average no. of hours of bright sunshine per day	Daily mean temperature	Mean maximum temp. in Stevenson Screen.	Mean minimum temp. in Stevenson Screen	Highest recorded temp.	Lowest recorded temp.	Mean min. temp. on grass	Mean relative humidity	Mean maximum relative humidity	Mean minimum relative humidity	Mean vapour pressure in inches of mercury.
		°F	°F	°F	°F	°F	°F	per cent	per cent	per cent	
January ...	10.0	73.9	82.9	66.7	94.0	53.1	58.7	68	74	54	0.571
February...	10.3	74.4	82.9	67.2	96.5	53.2	59.7	68	74	57	0.581
March ...	10.0	78.2	85.8	71.6	100.7	60.4	65.1	72	80	64	0.696
April ...	10.5	81.7	88.5	75.7	99.9	66.4	70.7	74	81	66	0.801
May ...	10.7	84.3	90.8	79.3	96.2	71.7	76.2	74	79	66	0.864
June ...	5.9	83.0	88.3	78.4	98.6	70.1	76.6	81	84	76	0.909
July ...	2.4	80.9	85.4	76.5	91.0	71.5	75.2	85	86	82	0.891
August ...	3.4	80.1	84.9	75.9	89.6	72.0	74.3	84	86	81	0.862
September	5.6	80.0	85.3	75.5	94.8	94.8	73.3	83	87	78	0.852
October ...	7.9	81.0	88.7	75.4	97.5	68.5	70.5	78	84	68	0.829
November	9.3	79.0	89.2	72.3	96.0	62.8	64.7	70	77	56	0.692
December	9.7	75.0	86.4	68.5	94.3	55.3	60.2	68	74	52	0.601
Annual mean		79.3	86.6	73.6			66.6	75			.762

The means are the averages of the values for all the hours of the day. The annual normal temperature of Bombay is 79.°3 F, the highest monthly mean being 84.°3 F in May and the lowest 73.°9 F in January. The annual march of temperature is shown in Fig. 2 in which five-day normals have been plotted.

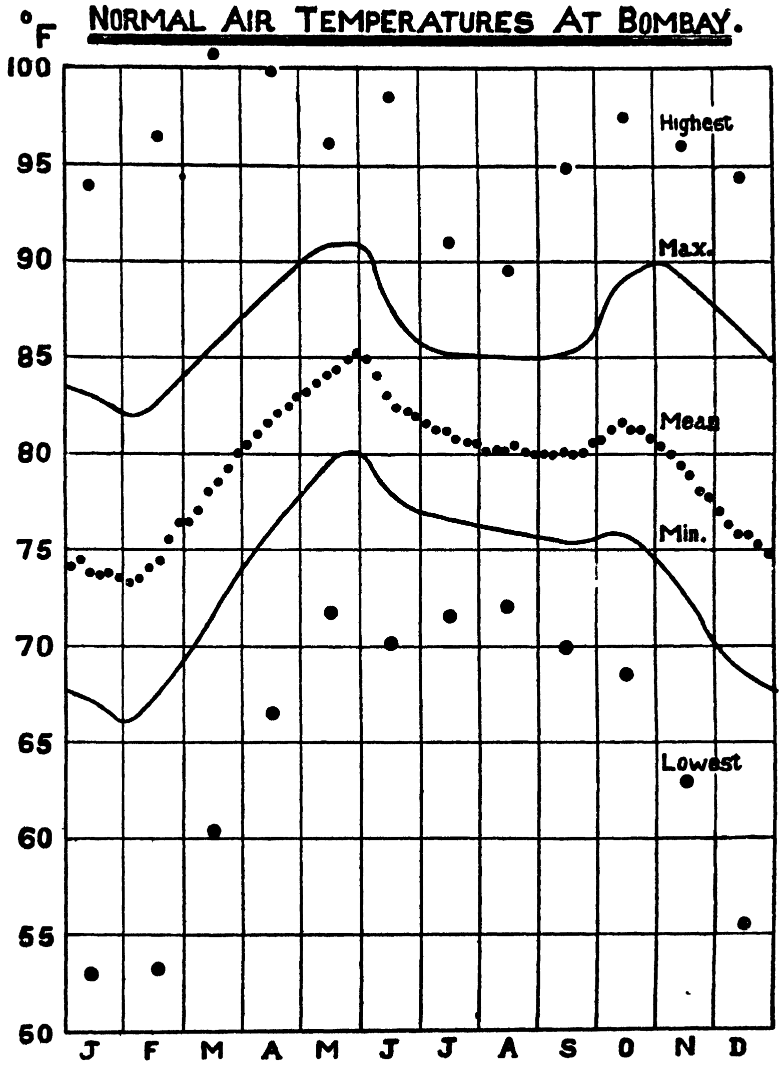

Fig. 2.

In the same figure are also shown the maximum and minimum temperatures and the highest and lowest temperatures recorded in each month. It will be seen that the coldest days occur normally towards the end of January and the hottest in the last week of May just before the onset of the monsoon. The temperature very near the surface of the ground is generally lower in the early mornings and higher in the afternoons owing to the effect of radiation on and from the ground. As a consequence, plants of low growth are subjected to greater ranges of temperature than those indicated by the maximum and minimum thermometers in Stevenson Screens. The monthly mean temperatures recorded by a grass minimum thermometer exposed a couple of inches above ground on closely cut lawn are also given in Table 3.

The arrival of the monsoon causes a large and welcome fall of temperature. This continues till the end of the monsoon, but there is again a rise in the mean temperatures in the first half of October after the withdrawal of the monsoon. On most days in the dry season a northwesterly sea-breeze blows in the afternoon, producing a marked fall of temperature and increase of relative humidity. The daily range of temperature is largest in the dry sunny months November to February when the maximum is about 6°F above the daily mean temperature and the minimum 4 to 5°F below it. The lowest mean ranges occur in July and August when the skies are mostly clouded and the atmosphere is nearly saturated with moisture. The mean range in these months is only 3 to 4°F. The minimum temperature of the day generally occurs within half an hour after sunrise and the maximum in the afternoon at about 14½ hours.

The climate of Bombay has a reputation for being monotonously uniform. This is to a large extent true. The day to day variation of temperature is smallest in April and May when the temperature is highest and the humidity is high and the monotony is therefore most keenly felt. Considering the year as a whole, the day to day variability of temperature is greatest in the period 1st January to 15th March and least in May. There is another period of minimum variability after the close of the monsoon in the latter half of September and the first half of October.

The annual mean relative humidity of the air at Bombay is 75 per cent. The highest mean humidity is in the rainy months July and August when it reaches 85 per cent and the lowest in December to February when it goes down to 68 per cent. On rare occasions in the dry season, the humidity goes down to as low values as 15 per cent, but they last only for a few hours.

In table 4 are given the mean diurnal variations of temperature and relative humidity in the months January, April, July and October,

TABLE 4

NORMAL DIURNAL VARIATION OF TEMPERATURE AND RELATIVE HUMIDITY

Hour (local time)	January		April		July		October	
	T °F	H %	T °F	H %	T °F	H %	T °F	H %
	73.9+	68+	81.7+	74+	80.9+	85+	81.0+	78+
0	-2.4	+ 5	-2.1	+5	-0.7	+1	-2.0	+4
1	-2.8	+ 6	-2.4	+5	-0.9	+1	-2.3	5
2	-3.1	+ 6	-2.7	+6	-1.0	+1	-2.5	5
3	-3.5	+ 6	-3.1	+6	-1.1	+1	-2.8	5
4	-3.9	+ 5	-3.4	+7	-1.1	+1	-3.1	5
5	-4.3	+ 5	-3.7	+7	-1 3	+1	-3.3	5
6	-4.5	+ 5	-3.8	+7	-1.2	+1	-3.5	6
7	-4.7	+ 5	-2.4	+5	-0.9	+1	-2.9	5
8	-3.3	+ 3	-0.5	0	-0.3	+1	-1.5	2
9	-1.5	- 1	+1.0	-3	+0.2	0	-0.1	- 1
10	0.8	- 5	2.3	-5	0.9	-1	1.6	- 4
11	2.9	-10	3.1	-6	1.3	-2	2.9	- 8
12	4.7	-14	3.8	-7	1.5	-2	3 9	-10
13	5.6	-14	4.1	-7	1.7	-3	4.3	-10
14	5.9	-11	4.3	-8	1.8	-3	4.5	-10
15	5.7	- 9	4.0	-8	1.5	-3	4.2	- 8
16	5.0	- 7	3.5	-7	1.1	-2	3.6	- 7
17	3.4	- 3	2.4	-5	0.7	-2	2.1	- 4
18	1.8	+ 1	0.7	-4	0.1	-1	0.9	- 1
19	0.9	+ 3	0.3	+1	-0.3	0	0.1	+1
20	0.5	+ 3	-0.7	+2	-0.3	0	-0.3	2
21	-0.3	+ 4	-1.1	+3	-0.5	0	-0.7	2
22	-1.1	+ 3	-1.3	+4	-0.5	0	-1.2	3
23	-1.9	+ 4	-1.7	+5	-0.7	1	-1.7	3

RAINFALL

The rainfall of Bombay is mainly confined to the four months June, July, August and September. Of the annual normal of 70.5 inches, 67.1 inches fall in these four months. The monsoon usually arrives at Bombay between the 1st and 10th June. There have been only two occasions during the last 90 years when the monsoon arrived earlier than the 25th May and only two occasions when it was as late as the 20th June. The first advance of the monsoon is often accompanied by a depression in the Arabian Sea. The rainfall normals in each month are shown in Table 5. July is the rainiest month.

Fig. 3 showing the mean rainfall amounts on each day of the year clearly brings out three periods of maximum intensity of rainfall.

TABLE 5—RAINFALL IN BOMBAY

Month	Normal number of rainy days	Normal rainfall in inches	Maximum rainfall in the month with year of occurrence	Minimum rainfall in the month with year of occurrence
January ...	0.1	0.09	2.2 (1871)	0
February ...	0.2	0.06	1.7 (1917)	0
March ...	0.1	0.04	1.5 (1918)	0
April ...	0.1	0.04	1.6 (1898)	0
May ...	0.8	0.68	11.2 (1818)	0
June ...	14.7	19.7	43.5 (1886)	5.1 (1885)
July ...	22.5	23.9	59.3 (1907)	4.3 (1918)
August ...	19.6	13.2	36.6 (1892)	3.4 (1882)
September ...	13.6	10.3	43.8 (1930)	1.6 (1896)
October ...	2.7	2.1	16.1 (1917)	0
November ...	0.5	0.39	5.5 (1847)	0
December ...	0.1	0.05	1.1 (1884)	0
Annual mean ...	75	70.5		

The maximum rainfall recorded in a day was 21.6 inches on 10.9.1930. The maximum recorded fall in an hour is 4.22 inches.

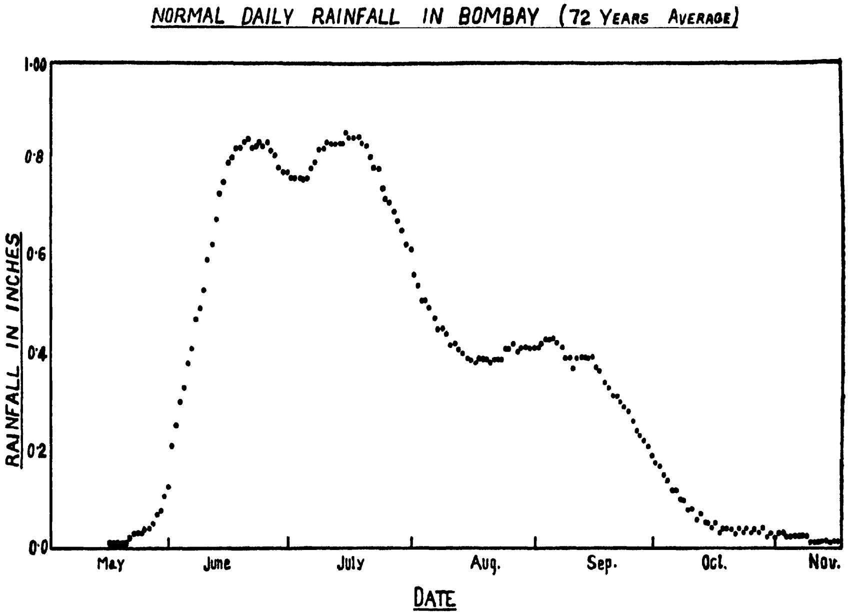

Fig. 3

The heavy rainfalls during the monsoon occur in spells. They are associated (1) with the advance of the monsoon from south to north, (2) with monsoon depressions which form or develop at the head of the Bay and move westwards towards the Central Provinces and Gujarat and (3) with its retreat from N. India towards the south. During times of weak monsoon the rainfall is intermittent, occurring in sharp showers two or three times during the day and unevenly distributed as regards locality even within the limits of Bombay. These rains are usually accompanied by squally winds. The rainfall in October and November is associated with post-monsoon storms from the Bay of Bengal or the Arabian Sea.

Thunderstorms are rare when the monsoon is well established. A few days before the onset of the monsoon, afternoon thunderstorms are common and the beginning of monsoon is usually attended with a good thunderstorm. Afternoon thunderstorms are also common at about the time of withdrawal of the monsoon.

There are of course considerable variations in the rainfall from year to year. The highest annual rainfall recorded during the last 90 years is 115 inches and there have been four years when the rainfall exceeded 100 inches. The lowest recorded rainfall is 33.4 inches and the amount was less then 40 inches in four years. In 48 out of the 90 years, the rainfall amount lay between 60 and 80 inches. The annual totals of rainfall in each of the years 1846 to 1937 are shown graphically in Fig. 4.

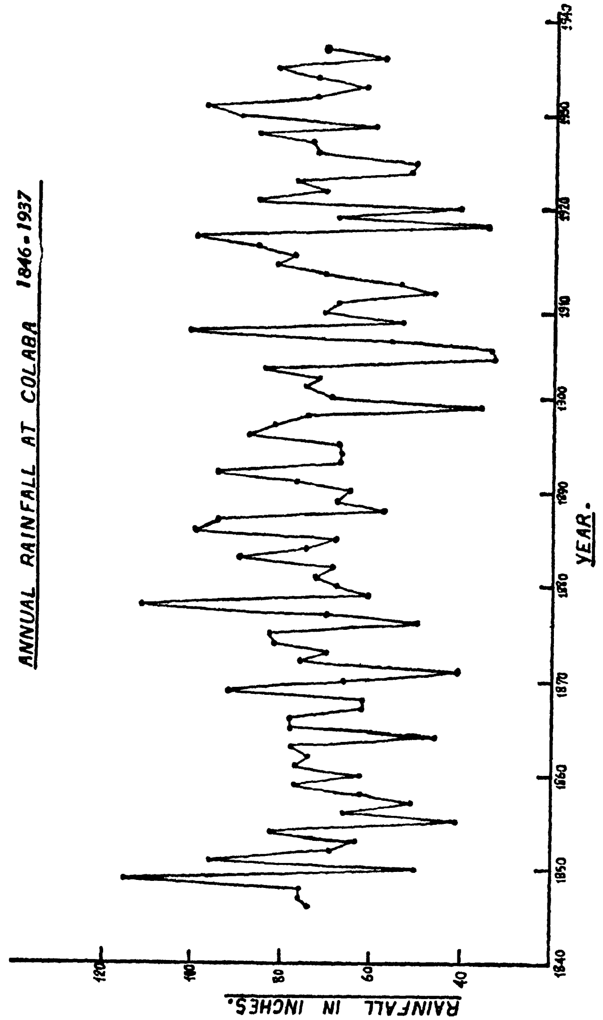

Fig. 4

It may be of interest to give here the monthly normal rainfall data of a few stations near Bombay.

Station	Jan.	Feb.	Mar.	Apr.	May	Jun.	July	Aug.	Sep.	Oct.	Nov.	Dec.	Annual
	″	″	″	″	″	″	″	″	″	″	″	″	″
Bombay (Colaba)	0.1	0.1	0.	0.	0.7	19.7	23.9	13.2	10.3	2.1	0.4	0.1	70.5
Thana	0.2	0.	0.1	0.	0.9	21.7	36.2	22.1	12.7	3.1	0.4	0.1	97.5
Kalyan	0.2	0.1	0.	0.	0.5	19.2	37.3	23.8	11.8	3.3	0.3	0.1	96.6
Karjat	0.1	0.	0.1	0.1	0.7	22.1	48.6	34.5	16.7	4.5	0.5	0.1	128.0
Lonavla	0.1	0.	0.	0.2	1-0	27.7	66.4	46 9	19.4	3.9	0.9	0.1	166.7
Poona	0.1	0.1	0.1	0.1	1.4	5.3	7.2	3.7	5.1	4.0	1.1	0.2	28.4
Mahābaleshwar	0.1	0.1	0.1	1.3	1.9	46.2	104.8	74.9	28.3	6.0	1.5	0.3	265.5

Typical charts of self-recording instruments showing the diurnal variation of weather in different months.

In Figures 5 and 6 are reproduced the self-recording instrument charts of wind velocity and direction, rainfall and dry and wet-bulb temperatures on a few typical days in the months January, May, June, July and November. They show, much better than mere verbal description, the usual diurnal variations of weather in each of these months.

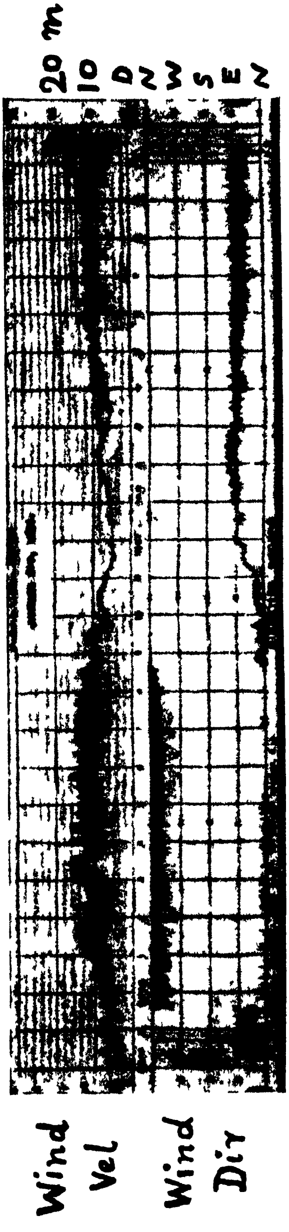

Fig. 5a—A day in January with moderate north-north-westerly winds in the afternoon and easterly land winds in the forenoon.

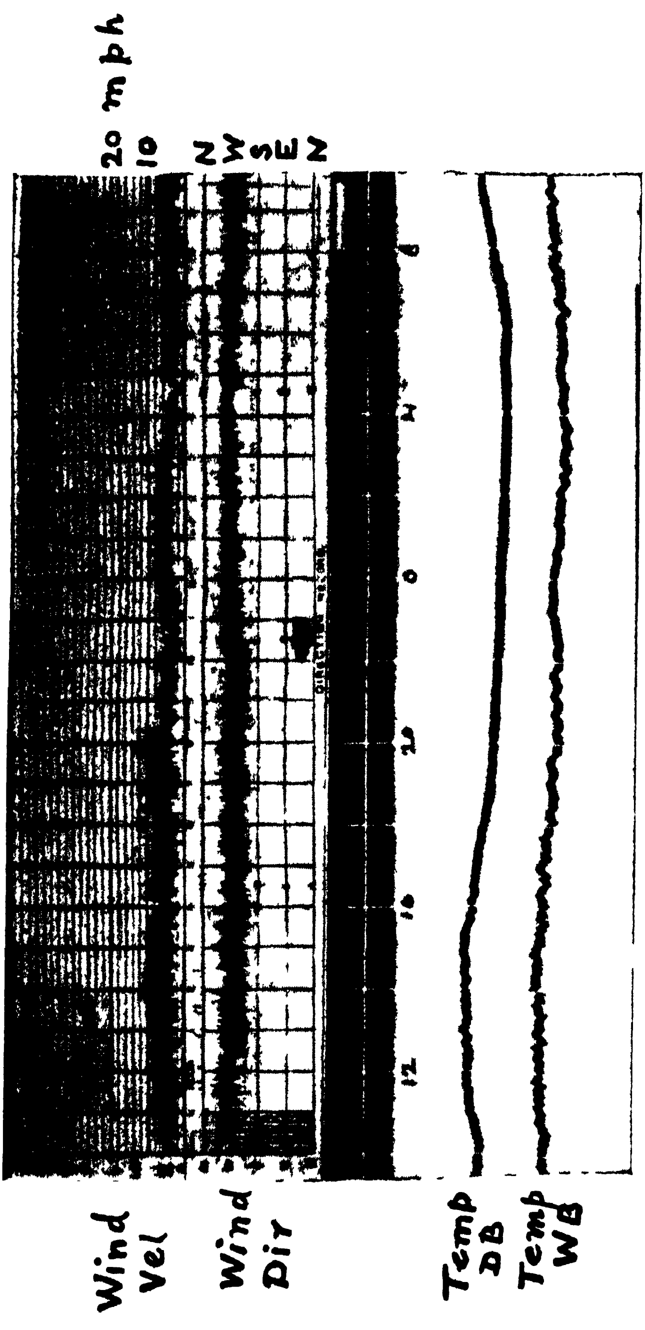

Fig. 5b—Wind and temperatures on a day in May with westerly winds throughout the day and night.

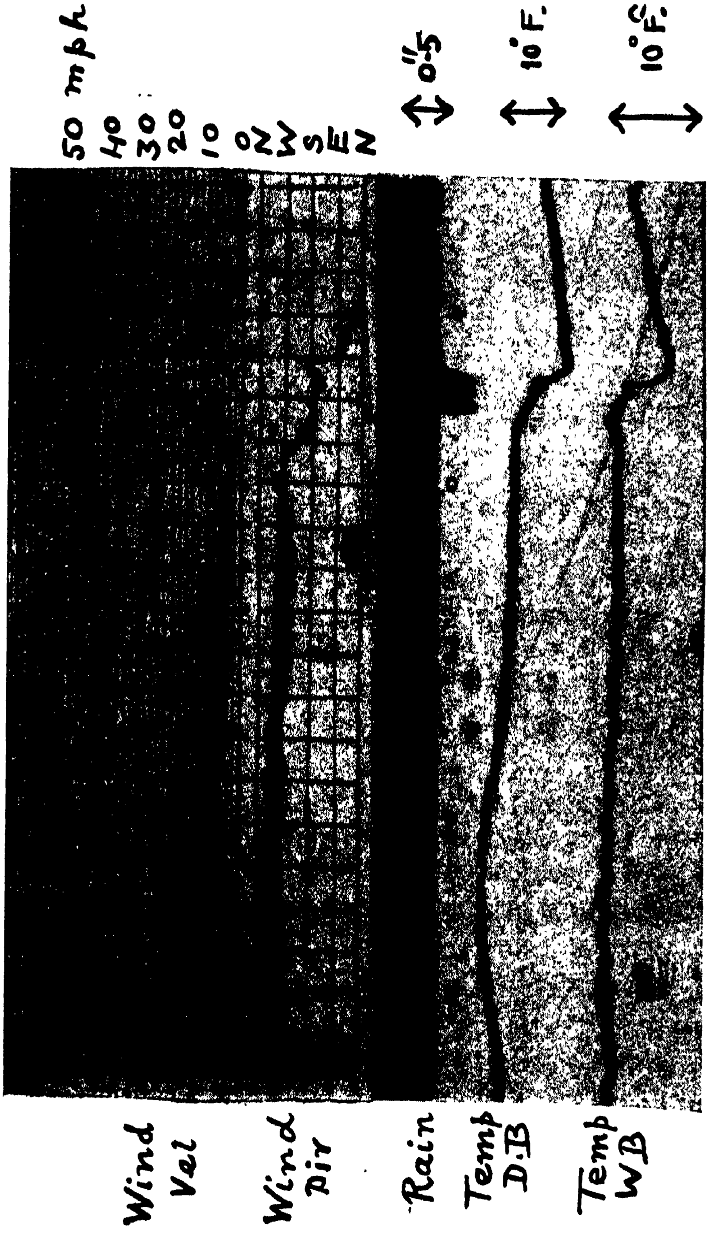

Fig. 5c—Thunderstorm at about 2 a.m. on June 12, 1937 heralding the onset of the monsoon. Max. wind velocity 53 miles per hour.

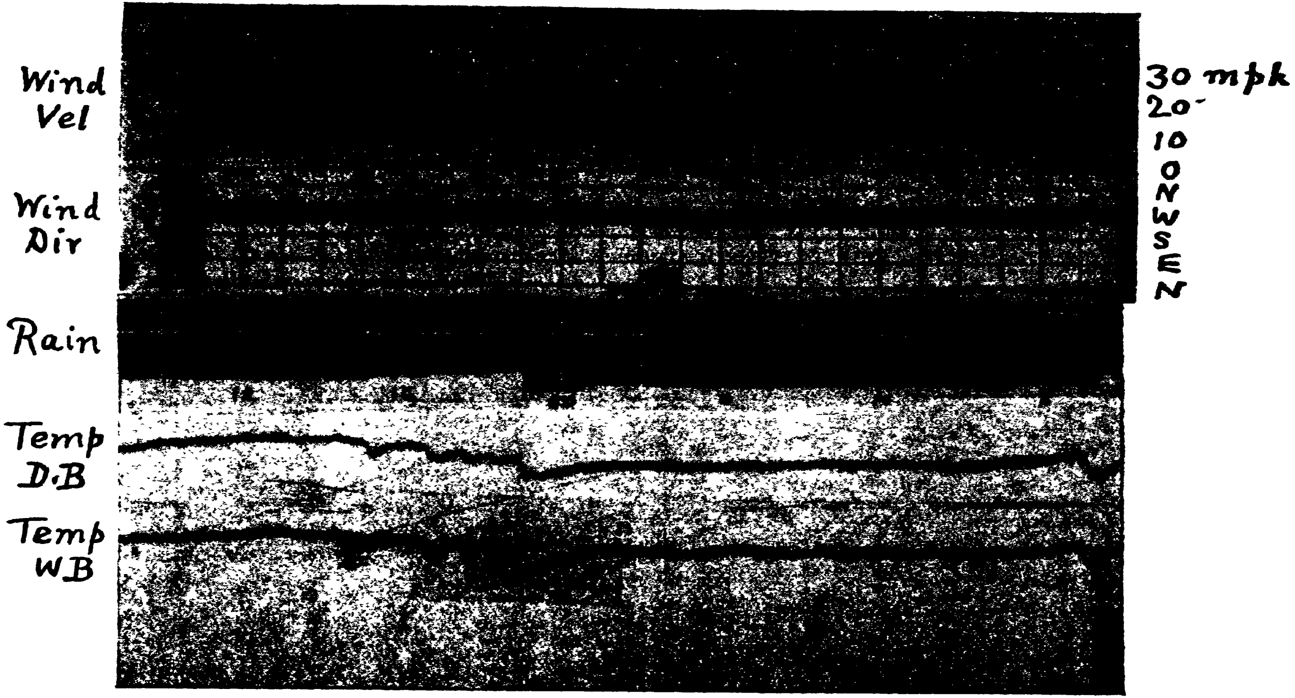

Fig. 6a—Typical monsoon weather with strong, gusty wind from the west and intermittent rainfall. June 30—July 1, 1937.

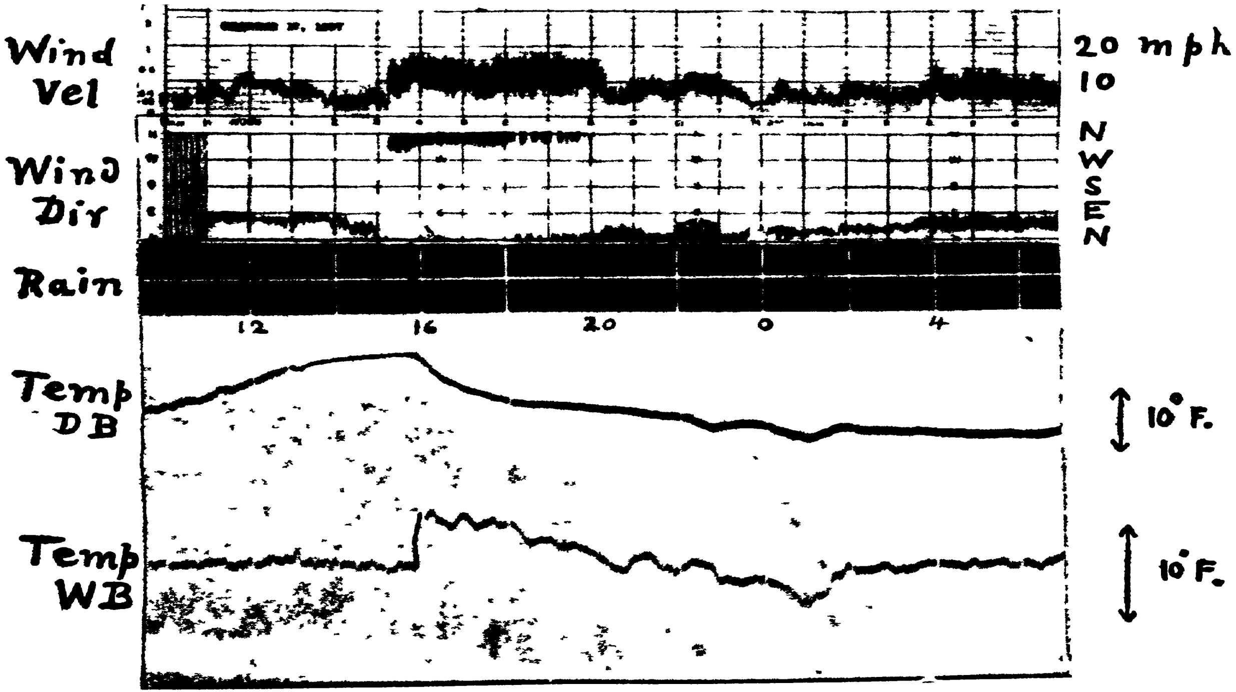

Fig. 6b—Wind and temperature on a clear November day with afternoon sea-breeze and night land-breeze. Note the fall of dry bulb and rise of wet bulb temperatures some minutes after the wind shifts to N. N. W.

The charts for June 11-12, 1937 (Fig. *5c*) show an afternoon thunderstorm which heralded the onset of the monsoon that year. The maximum speed of wind accompanying the thunderstorm was 52 miles per hour. The charts for November 17, 1937 (Fig. *6b*) show the large and sudden drop of temperature and rise of humidity which often accompany the onset of sea-breeze in the drier months.

I am thankful to Mr. D. L. Chaudhuri M.Sc. and Mr. S. Jagadish for considerable help in preparing the tables and diagrams.

PHOTOREDUCTION OF FERRIC COMPOUNDS.

By

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Many organic substances decompose when they are exposed to light in the presence of ferric salts. It has been found that in this process the organic compound is oxidised and the ferric salt is reduced to the ferrous state. The earliest observation on the subject was made in the eighteenth century by Bestucheff, the Prussian Chancellor, who noticed that the colour of a solution of ferric chloride dissolved in alcohol is discharged when it is exposed to sun light. Since then a large number of these photochemical reactions have been studied mainly from two points of view: (i) to study the course of oxidation of organic substances and to isolate the various products formed during the reaction and (ii) to study the chemical kinetics of the reactions and to examine the applicability of the laws ot photochemistry to them.

Eder (Sitz. Wien Acad., 1880, 82, 606) investigated the action of sun light on an aqueous solution of ferric chloride in the presence of oxalic, citric, tartaric and other organic acids and found that it is slowly reduced and carbon dioxide is given off. Ferric oxalate was also found to decompose to ferrous oxalate with the evolution of ·carbon dioxide but ferric acetate and ferric formate were not affected. Jodlebauer (Zeit. physikal Chem., 1907, 59, 513) studied the action of light on solutions of ferric oxalate and ferric tartrate and found that in both cases carbon dioxide is evolved and ferrous salts are precipitated. The photochemical action is retarded by oxygen although the amount of carbon dioxide liberated remains the same. He considers that in the presence of oxygen some intermediate compound is formed but no information regarding its nature could be obtained.

Benrath (J. pr. Chem., 1905, 72, 220) extensively studied the photo-reduction of ferric salts in the presence of several organic substances. He mixed sublimed ferric chloride with methyl and ethyl alcohols, trioxy-methylene, ether, formaldehyde and acetaldehyde and formic and acetic acids, in a sealed tube and exposed them to bright sun light. On analysing he found that the products formed in the case of methyl and ethyl alcohols are alkyl chloride aldehyde, hydrogen chloride and ferrous chloride carrying four molecules of alcohol or of water according as the alcohols are anhydrous or contain some moisture. Trioxymethylene was found to yield an unstable dark violet additive compound and ether is oxidised to acetaldehyde hydrochloride, hydrogen chloride, a mixture of butane and ethyl chloride and ferrous chloride: The aldehydes in presence of water yield the corresponding acids, hydrogen chloride and hydrated ferrous chloride but if anhydrous acetaldehyde is used, resins are formed. Formic acid leads to the formation of carbon dioxide and hydrochloric acid while acetic acid forms a rose coloured powder. Later on Benrath found (J. pr. Chem., 1912, 86, 336) that when an aqueous solution of formaldehyde containing ferric chloride is exposed to sun light it is oxidised to glyoxal. Under similar circumstances amyl alcohol is oxidised to acetone and acetaldehyde, whilst fatty acids either remain unaffected or they are oxydised very slowly. In nitric acid solution containing ferric nitrate an exposure to sun light causes the oxidation of organic acids, ethyl alcohol and acetone while nitric acid is reduced to nitrogen and ammonia. When aqueous solutions of tartaric, citric and glycollic acids mixed with iron alum are exposed to sun light in sealed tubes, they are oxidised to some acids which could not be isolated but only their presence could be detected or surmised, and carbon dioxide is given off.

Neuberg (Biochem. Zeit., 1910, 29, 279) examined the action of light on a large number (forty five) of organic substances in the presence of ferric sulphate and found that all of them show degradation, for example, alcohols are changed to aldehydes and benzoic acid is oxidised to salicylic acid. He also estimated in some cases the amount of products formed during the reaction. Neiger and Neuschul (Zeit. physikal chem., 1936, 177, 355) observed that ferric gluconate is reduced when its aqueous solution is exposed to sun light, to ferrous gluconate which separates out in crystalline form.

Other important workers on the subject are Baudisch, Puxeddu, Fry and Germe and Burt. Baudisch (Biochem. Zeit., 1918, 92, 189) found that in admixed solutions with quinol, acetacetone, acetoacetic ester, salicylaldehyde, salicylic acid, catechol and o-carboxylic acid, ferric chloride is reduced only when it is exposed to sun light or to light from a mercury quartz lamp. Puxeddu (Gazetta, 1920, 50, 154) observed that exposure to direct sun light of a dilute solution of ferric chloride in pure anhydrous ether brings about an instantaneous reduction of the salt to ferrous chloride. The liberated chlorine partly chlorinates the ether and partly oxidises it to aldehydes which undergo polymerisation to a certain extent. If the solution of ferric chloride is a concentrated one, the rate of reduction is slow and a brownish black insoluble organic compound containing iron is obtained. He separated the compound (cf. Gazz. Chim. Ital., 1920, 1, 153) and found that its composition varies with the conditions of the experiment. On exposing the liquid above the precipitate to sun-light for about a month he found that a mixture of di-and tri-chloro ethers is obtained. Fry and Germe (Univ. Cincinnati Ind. Eng. Chem., 1928, 20, 1392) found that when pharmaceutical solutions containing citric acid and ferric compounds are exposed to light they readily decompose. Carbon dioxide is evolved in this process and the acid is oxidised. Burt (J. Amer. Pharm. Assoc., 1928, 17, 650) examined the action of light on solutions of ferric hydroxide dissolved in citric acid and found that it decomposes with the evolution of carbon dioxide and simultaneous formation of acetone. He also found that the reaction ceases when all the ferric ions are reduced and that three molecules of carbon dioxide are formed for every molecule of acetone.

The property of ferric chloride in bringing about the photo oxidation of organic compounds has found application in the study of problems of photosynthesis. Dhar and Sanyal (J. Phys. Chem., 1925, 29, 926) found that if carbon dioxide is passed in water containing ferric chloride in presence of sun light for six hours, formaldehyde is formed and the ferric salt is reduced. Dhar, Rao and Atma Ram (Trans. Farad. Soc., 1927, 27, 554) and Rajvanshi and Dhar (J. Phys. chem., 1932, 36, 575) found that maximum polymerisation of formaldehyde to sugars takes place when three per cent solution of formaldehyde containing ferric choride is exposed to sun light for 30-60 hours. The former authors also found that the temperature coefficient of polymerisation is 1.26.

For the same reason ferric salts are used as photosensitizers in numerous reactions. Kunz, Krause and Manicke (Ber. pharm. Ges., 1920, 32, 209) found that oxalic acid decomposes in arc light in presence of ferric chloride. Under identical conditions lactic acid is oxidised with the formation of acetaldehyde and mercuric chloride in Eder's solution is reduced in the presence of ferric salts (cf. Kastle and Beatty, J. Amer. Chem. Soc., 1900, 24, 182). These reactions have been shown to proceed in two stages; the ferric salt is reduced in the first stage and is reoxidised in the second. Winther (Zeit. Wiss. Phot., 1909, 7, 409; 1909, 8, 197, 1911, 9, 205) studied thoroughly the catalytic action of ferric salts in the photochemical reaction between mercuric chloride and ammonium oxalate and showed that these salts accelerate the reaction in small concentrations only; large concentrations completely inhibit the photochemical reaction. By taking absorption spectra of Eder's solution containing ferric salts he showed that photochemical sensitivity to long wave-lengths is due to the shift of the absorption from 3130 A° to 5000 A° which is caused by the presence of ·ferric salts. He confirmed this view by showing that the same light sensitivity can be caused by certain dyestuffs which absorb these wave-lengths.

Eder (loc. cit.) was the first to study the photoreduction of ferric salts in a quantitative manner. He estimated the quantity of ferrous salt formed in a minute when a ferric salt underwent reduction by the action of sun light in the presence of several organic acids and thus obtained comparative values for the reducing efficiencies of these acids. Ross (J. Amer. Chem. Soc., 1906, 28, 790) estimated the reduction of ferric chloride, ferric sulphate and ferric nitrate in the presence of cane sugar by ultra-violet light and found that from solutions of the same concentrations the ferric chloride is reduced most and ferric nitrate the least. He showed by optical methods that the differences in the photochemical activity are due to the differences in the absorption of light by solutions of the same concentrations of the above named salts. He further found that the amount of reduction increases with an increase in the amount of sugar in the solutions and is approximately proportional to time.

The rate of reduction of penta carbonyl of iron dissolved in pyridine and light petroleum was studied at ordinary temperatures in sun light by Dewar and Jones (Proc. Roy, Soc., 1907, 79, 66) by observing the change in pressure at different intervals and the reaction was found to be approximately unimolecular. The photo-decomposition of $Fe(CO)_5$ was further studied by Eyber (Zeit. physikal Chem., 1929, 144, 1) in the vapour phase at the ordinary temperature. He found that the reaction velocity is directly proportional to the concetration of the vapour and to the intensity of the incident light. He represents the complete reaction as follows :

$$\mathrm{Fe\,(CO)_5} + h\nu \rightarrow \mathrm{Fe\,(CO)_5}^{*} \text{ (activated)}$$

$$\mathrm{Fe\,(CO)_5}^{*} + \mathrm{Fe\,(CO)_5} \rightarrow \mathrm{Fe_2\,(CO)_9} + \mathrm{CO}$$

Thomson and Garratt (J. C. S., 1934, 524), however, explain the mechanism of the same reaction in a different manner. According to them the decomposition takes place as

$$\mathrm{Fe\,(CO)_5} + h\nu \rightarrow \mathrm{Fe\,(CO)_4} + \mathrm{CO}$$

$$\mathrm{Fe\,(CO)_4} + \mathrm{Fe\,(CO)_5} \rightarrow \mathrm{Fe_2\,(CO)_9}$$

Benrath (J. pr. Chem., 1909, 80, 283) employed physical instead of the chemical methods for estimating the amount of reduction of ferric salts in presence of light. He found that the change in the density of the solution could be used to measure the change in the concentration of the reacting substance and found that $A \times 10^7/t$ where A represents the change in density is practically constant. Later on he found (Annalen, 1911, 382, 222) that the change in the electrical conductivity of the exposed solution at different intervals can be used to estimate the amount of reduction of ferric chloride dissolved in ethyl alcohol: the increase in conductivity per minute rises rapidly and finally becomes constant. In this manner he studied the photo-reduction of ferric chloride in the presence of tartaric, citric and oxalic acids and obtained relative values for the reducing action of these acids (cf. Benrath. Zeit. physikal Chem., 1910, 74, 115). He also found that the reduction of ferric chloride by hydroxy acids in acetone solution is much slower than in water under similar circumstances.

Previously Long (J. Amer. Chem. Soc., 1897, 19, 683) had employed the measurement of conductivity as a means to determine the amount of reduction from time to time when a solution containing ferric alum and sugar is exposed to bright sun light. He found that the speed of the reaction is an accelerated one, the acceleration being caused by the sulphuric acid liberated as reduction progresses, and it can be represented by the equation $\frac{dx}{dt} = k\,(A-x)\,(B-x)$ where A and B represent the initial amounts of the ferric salt and the sugar and x the amount of reduction at different intervals.

Puxeddu and Vodret (Gazetta, 1922, 52, 229; Gazz. Chim. Ital., 1922, 52, 229) studied the velocity of reduction of ferric chloride in ethereal solution in sun light and in light from an arc lamp. They estimated the amount of reduction by titrating the amount of ferrous chloride with potassium permanganate in presence of a few c. cs. of Zimmermann's solution and found that the reduction is completed in one hour and it follows the equation for unimolecular reactions. But at the same temperature the decomposition is much slower in the light of the arc than in sun light.

Benrath (loc. cit.) was, however, the first to establish that in the photo-reduction of ferric chloride in presence of organic substances, light does not act as a catalyst but as an actual generator of chemical energy. On exposing solutions of ferric chloride dissolved in alcohol in quartz vessels to light from a mercury vapour lamp he found that the quotient t/c, where c is the concentration of the solution and t the time required for its decolourisation, is nearly constant. He thus proved that the light energy required to reduce a definite quantity of ferric chloride is nearly constant and is independent of the concentration of the ferric chloride solution. Bolin (Zeit. physikal Chem., 1914, 87, 490) also found that light does not act catalytically in the photo-oxidation of lactic acid by ferric sulphate.

Lemoine (Compt. rend., 1895, 121, 817) examined the effect of the intensity of light on the chemical change produced when a mixture of ferric chloride solution and oxalic acid is exposed to sun light and found that there is a direct proportionality between the two. Further he found that the amount of reduction is the same whether the exposure of a given total duration is intermittent or continuous. More exhaustive work was however done by Winther and Oxholt-Howe (Zeit. Wiss. Photochem., 1914, 14, 196) who studied the effect of monochromatic light of different wave-lengths on the rate of reduction of ferric chloride in the presence of equimolecular quantities of the ammonium salts of oxalic, succinic, tartaric, citric and acetic acids and found that the rate remains constant during the course of the reaction. Further they found that for a given concentration, the sensitiveness increases as the absorption coefficient diminishes and that the number of the reacting molecules per quantum of absorbed energy is in all cases greater than unity. They explain their results on the supposition that the reacting solutions contain at least two different light absorbing molecular species containing ferric ion, one of which is photochemically active while the other is not and the light energy absorbed by it is transformed into heat energy. According to Ghosh and Mitra (J. Indian Chem. Soc., 1928, 5, 191) who measured the extinction coefficients of solutions of ferric chloride containing different organic acids during exposure to light, an intermediate complex is formed between the ferric chloride and the organic acid.

Padoa and Miss Vita (Gazetta, 1924, 54, 147) also studied the effect of wave-length on the photo-reduction of ferric chloride in the presence of oxalic acid and some catalysts. They employed light from an arc lamp filtered through various filters and found that in the absence of a catalyst the spectral region over which the action takes place is limited but the sum of the effects in the blue and violet is 1.123 times that of the white light. The zone of active radiations is widened in the presence of quinine hydrogen sulphate and the total action in blue, green and violet light is 2.125 times that in the white light.

A thorough study of the reduction of ferric chloride in the presence of mandelic, lactic and tartaric acids was made by Ghosh and Purukayastha (J. Indian Chem. Soc., 1929, 6, 827) in visible light from a point-o-lite lamp. They found that the order of the reaction is zero molecular and the temperature coefficient of the reaction is unity. In accordance with the derivation from the theory developed by Turner (Phys. Rev., 1924, 23, 464) they found that the reciprocal of the velocity of the reaction plotted against the reciprocal of the concentration of the ferric chloride solution is a straight line. From the slope and the intercepts of this line they calculated an approximate value of the life of the excited molecule. Further they measured the quantum efficiencies of the reaction at various wave-lengths and found that they increased with the increase in the frequency of the exciting radiation. Lal and Gangully (Zeit. Anorg. Chem., 1936, 229) studied the reduction of solutions of ferric hydroxide dissolved in organic acids in light from a mercury vapour lamp. They found that the reaction is approximately zero molecular although a small distinct fall in values of x/t takes place during the progress of the reaction. The reduction is considerably accelerated in the presence of thorium, uranium, copper and zirconium salts; thorium salts being the best catalysts. The velocity of reaction is found to increase with an increase in the intensity of light and two quanta are necessary for the reduction of one molecule of ferric salt.

Ionsen and Beardeamm (Bul. Soc. Chem. Rumania, 1935, 17, 297) studied the photo-reduction of aqueous solution of ferric chloride in presence of β naphthol. They found that the reaction becomes appreciable in the presence of HCl and is unimolecular with respect to both the reactants. They, therefore, conclude that the photo-reduction of ferric chloride takes place through intermediate reactions.

Spicer (Trans. Farad. Soc., 1935, 31, 1706) employed the radioactive radiations to study the reaction of aqueous and ethereal solutions of ferric chloride. They found that complete reduction occurs when these solutions are exposed to α rays, but the reduction is partial when solid anhydrous ferric chloride is employed. No reduction takes place when aqueous solutions of ferric chloride are exposed to β and γ rays.

Allmand and Webb (J. C. S., 1929, 1531) studied the photolysis of potassium ferrioxalate in monochromatic light of wave-lengths lying between 313–436 $\mu\mu$ and found that the quantum efficiency of the reaction is of the order of unity and that it decreases with an increase in wave-length. Further they found that for certain concentration limits the quantum efficiency is independent of the concentration of the photolyte. Allmand and Young (J. C. S., 1931, 3079) found that the temperature coefficient of the photolysis of potassium ferri oxalate between 22°–55° rises from 1.029 at 3130 A° to 1.060 at 4360 A°. They further found that the effect of the two monochromatic radiations acting simultaneously is greater than that calculated additively and suggested the following mechanism to represent the mode of the photo-reaction.

$$\mathrm{Fe}^{\cdots} + h\nu \longrightarrow \mathrm{Fe}^{\cdots\,*}\ \text{(activated)}$$

$$\mathrm{Fe}^{\cdots\,*} + \mathrm{C_2O_4}'' \longrightarrow \mathrm{Fe}^{\cdot\cdot} + \mathrm{C_2O_4}'$$

Or.

$$\mathrm{Fe}^{\cdots\,*} + \mathrm{H_2C_2O_4} \longrightarrow \mathrm{Fe}^{\cdot\cdot} + {}_2\mathrm{H} + \mathrm{C_2O_4}'$$

$$\mathrm{C_2O_4}' + \mathrm{Fe}^{\cdots} \longrightarrow \mathrm{Fe}^{\cdot\cdot} + {}_2\mathrm{CO_2}$$

The photo-reduction of ferric chloride has been systematically investigated by Prasad and co-workers. Prasad and Sohoni (J. Indian Chem. Soc., 1931, 8, 489) studied the kinetics of the reduction of ferric chloride dissolved in alcohols in visible light. *They found that the intensity of light has little effect on the velocity of photo-reduction of concentrated solutions; as a matter of fact, they observed less reduction in stronger light than in the weaker one. They also found that in some cases the reaction* conforms to the unimolecular law but in all cases it reaches a stationary stage after some time from the commencement of the reaction. The addition of water accelerates the reaction while the presence of electrolytes retards it and the temperature coefficient of the reaction lies between 1.00 and 1.15

Prasad and Limaye (J. Indian Chem. Soc., 1933, 10, 91 and 101) studied the photo-reduction of ferric chloride dissolved in anhydrous alcohols in sunlight and in light from a thousand candle power lamp. They found that the reaction takes place in two stages, the order of the reaction in sunlight is zero molecular in the first stage and unimolecular in the second while in artificial *light it is zero molecular in both the stages. The measurement of conductivities of solutions after different intervals of exposure to sunlight gives no indication of the change in the mode of the* reaction but the measurement of extinction coefficient of solutions exposed to light shows a remarkable change after four hours when the second stage of the reaction sets in. The temperature coefficient of the reaction varies between 0.92 to 2.4 while the quantum efficiency from 0,6 to 4.0.

The photo-reduction of ferric chloride dissolved in alcohols was further studied by Prasad and Mohile (Proc. Nat. Acad. Sci., 1936, 6, 261) in light from a quartz mercury vapour lamp. They found that the reduction takes place in two stages and the order of the reaction is zero molecular in both the stages. They further found that the velocity of reduction is not independent of concentration of the solution of ferric chloride but it is given by the relation $\frac{d(FeCl_3)}{dt} = K(FeCl_3)^n$ where K and n are constants. Mohile (Thesis Bombay University 1935) showed the presence of ferric iron in a visibly completely decolourised alcoholic solution of ferric chloride and thus proved that a colourless complex containing ferric ion is formed in these solutions.

The .mechanism of the photo-reduction of ferric chloride dissolved in alcohols has been explained by Benrath (loc. cit.) on the assumption that the primary photochemical reaction is

$$2\,FeCl_3 + RCH_2OH \xrightarrow{h\nu} 2FeCl_2 + 2HCl + RCHO$$

Other products of the reaction are obtained by the secondary reactions between hydrochloric acid and the alcohol and the aldehyde

$$RCH_2OH + HCl \rightarrow RCH_2Cl + H_2O$$

$$RCHO + HCl \rightarrow RCHO,\ HCl.$$

This mode of reaction suggests that the molecules of both ferric chloride and alcohol get activated by the absorption of light and the collisions between these activated molecules bring about the primary photochemical reaction mentioned above. But this is impossible since alcohol does not absorb the white radiations and hence the alcohol molecules do not directly get activated.

The mechanism of the photo-reduction of aqueous solutions of ferric choloride in presence of aldehydes suggested by Benrath (J. Prakt. Chem., 1905, 72, 220) is

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

$$RCHO + HCl \rightarrow RCH(OH)Cl$$

$$RCH(OH)Cl + 2\,Fecl_3 \xrightarrow{h\nu} RCO\,Cl + 2\,FeCl_2 + 2HCl$$

$$RCOCl + H_2O \rightarrow RCOOH + HCl$$

In the above suggestion it is rather strange to find that the aldehydes which are well known reducing agents do not reduce the ferric chloride directly even in the presence of light.

The mechanism of the photo-reduction of ferric salts has been exhaustively discussed by Prasad, Mohile and Nigudkar

(J. Bom. Uni., 1936, 5, 142) from various probable points of view, such as, the mechanism suggested by Benrath, the formation of complex and its subsequent reduction, the dissociation of ferric chloride etc. They conclude that the best method of explaining the mode of these reactions is to suppose that either the ferric ions or the molecules of ferric chloride get activated by the absorption of light. In the former case the collisions between the activated ferric ions and molecules of alcohol give rise to molecules of hydrogen which cause the reduction of the ferric ions; in the latter case the collisions between the activated and unactivated molecules of ferric chloride cause the dissociation of ferric chloride as

$$\mathrm{Fe\,Cl_3} \xrightarrow{h\nu} \mathrm{Fe\,Cl_3}^{*} \text{ (activated)}$$

$$\mathrm{Fe\,Cl_3}^{*} + \mathrm{Fe\,Cl_3} \rightarrow 2\,\mathrm{Fe\,Cl_2} + \mathrm{Cl_2}$$

It should be noted that Audubert (J. Chem. Phys., 1927, 24, 357) who studied the photo-voltaic E.M.F. of the cell.

$$\mathrm{Pt}\ \left|\ \begin{matrix}\text{Solution of}\\ \mathrm{Fe\,Cl_3}\text{ exposed}\end{matrix}\ \right|\ \begin{matrix}\text{Solution of}\\ \mathrm{Fe\,Cl_3}\text{ unexposed}\end{matrix}\ \left|\ \mathrm{Pt}\right.$$

also concluded from his measurements that dissociation of ferric chloride takes place in the solution exposed to light. Hughes (Phil. Mag., 1912, 380) found that ferric chloride does not show any photo-electric effect and thus there is no possibility of ferric chloride decomposing as

$$\mathrm{Fe\,Cl_3} \xrightarrow{h\nu} \mathrm{Fe\,Cl_2}^{+} + \mathrm{Cl}^{-}$$

The dissociation of ferric chloride may, therefore, take place as

$$2\,\mathrm{Fe\,Cl_3} \xrightarrow{h\nu} 2\,\mathrm{Fe\,Cl_2} + \mathrm{Cl_2}$$

in which case chlorine in the molecular state is liberated according to the mechanism suggested above.

Other products of photo-reaction in presence of alcohol are

$$\mathrm{R\,CH_2\,OH} + \mathrm{Cl_2} \rightarrow \mathrm{R\,CHO} + 2\,\mathrm{HCl}$$

$$\mathrm{R\,CH_2\,OH} + \mathrm{H\,Cl} \rightarrow \mathrm{R\,CH_2\,Cl} + \mathrm{H_2O}$$

This mechanism can also be used to explain the photo-oxidation of aldehyde in the presence of ferric chloride, as

$$\mathrm{Cl_2} + \mathrm{H_2O} \rightarrow \mathrm{H\,Cl} + \mathrm{H\,Cl\,O}$$

$$\mathrm{R\,CHO} + \mathrm{H\,Cl\,O} \rightarrow \mathrm{H\,Cl} + \mathrm{R\,COO\,H}$$

$$\mathrm{R\,CHO} + \mathrm{H_2O} \rightarrow \mathrm{R\,CH\,(OH)_2}$$

$$\mathrm{R\,CH\,(OH)_2} + \mathrm{Cl_2} \rightarrow \mathrm{R\,COO\,H} + 2\,\mathrm{H\,Cl}$$

ABSTRACTS OF Ph. D. THESES

I—SCATTERING OF LIGHT BY A CLOUD OF LARGE WATER DROPS. BY. Y. G. NAIK.

1. The Theoretical investigations of Mie's theory by Blumar have been extended for 5 cases ($\alpha=4, 5, 7, 8$ and 10) of large sized drops. A comparison of all the scattering curves have been made along with one for $\alpha=12$ (after Rayleigh). It has been observed that the ratio of the intensity of scattered light in the forward direction to that in the backward direction is sufficiently large for all the values of α. The intensity fluctuations in different angles in the backward direction go on increasing rapidly till α reaches a value 10. For $\alpha=10$ the fluctuations are maximum and it appears that for larger sized particles these would soon disappear.

The planes of polarisation also alternate more and more rapidly as α approaches a value 10 and here again the alterations are maximum. They again appeared to vanish for larger values of α.

2. The theoretical results are compared with the experimental investigations of scattering of light in different directions for values of $\alpha=10.12$ and 43.73. lt is observed that the nature of both the curves is similar and that their lay/out coincides with the average lay/out of the theoretical curves for $\alpha=10$ and 12.

3. A comparison of the various theories of scattering has been made and it has been shown that the theory of Shoulejkin of the scattering of light being purely due to reflection and refraction is not borne out by the exact theory of Mie as well as by the experimental results.

4. The investigations of Pokrowsky are extended to a larger range of angles in the forward direction and it is found that the approximate theory as modified by him seems to fully account for the intensity distribution in the forward direction. The assumption that the refractivity must be small does not exclude the application of this theory of Rayleigh to water.

5. The nature of distribution of scattered light of different wave-lengths in different directions is experimentally observed for the first time and it is found that for larger drops the intensity varies directly as the fourth power of the wave-length.

6. The results of light transmission are explained on the basis of Houghton's approximate theory after Debye. The theoretical results of the scattering of light are also utilised to show the

exact changes that occur in the transmisson of light with the growth of the size of the drops. It is observed that the transmission suffers a few maxima and minima for values of α less than 12, but beyond this the transmission seems to go on increasing for all values of α.

AUTHOR

II—STUDIES IN COUMARINS.

BY N. M. SHAH.

Part I. Aluminium Chloride, a new reagent for the condensation of β-ketonic esters with phenols.

The condensation of β-ketonic esters with phenols has been extensively studied in recent years, the principal condensing agents used being conc. sulphuric (Pechmann reaction) acid and phosphoric anhydride (Simonis reaction). Other agents have been used to a much smaller extent, but the results obtained with these reagents are not usually of any particular interest.

It has been now found that anhydrous aluminium chloride acts as an efficient condensing agent for the condensation of β-ketonic esters with phenols. In this thesis the condensation of (i) resacetophenone and other phenolic ketones, (ii) simple phenols, with ethyl acetoacetate has been studied in the presence of this new condensing agent.

Section I. The condensation of resacetophenone and other phenolic ketones with ethyl acetoacetate: synthesis of 5-hydroxy-6-acyl-coumarins.

Though resacetophenone does not condense with ethyl acetoacetate in presence of sulphuric acid, the condensation takes place readily in presence of aluminium chloride with the exclusive formation of 5-hydroxy-6-acetyl-4-methyl-coumarin (I) in high yield. The constitution of (I) has been established by its synthesis by the Fries transformation of 4-methyl-5-acetoxy-coumarin and by the formation of 2′ : 4-dimethyl-3′-acetylchromono-7′ : 8′ : 6 : 5-α-pyrone and 3′-benzoyl-4-methyl-flavone-7′ : 8′ : 6 : 5-α-pyrone, by the Kostanecki acetylation and benzoylation respectively of (I).

The condensation of orcacetophenone in a similar manner gave 4 : 7-dimethyl-5-hydroxy-6-acetyl-coumarin, whose constitution was proved by its formation by the Fries transformation of 4 : 7-dimethyl-5-acetoxy-coumarin and the formation of 4 : 2′ : 5′-trimethyl-3′-acetyl-chromono-7′ ; 8′ : 6 : 5-α-pyrone,

Similar condensation of 2 ; 4-dihydroxy-benzophenone gave 5-hydroxy-6-benzoyl-4-methyl-coumarin, whose constitution has been arrived at by its synthesis by the Fries transformation of 5-benzoyloxy-4-methylcoumarin and by ring closure to 4-methyl-

4'-phenyl-coumarino-7' : 8' : 6 : 5-α-pyrone.

2-acetyl-resorcinol when similarly condensed gave 4-methyl-8-acetyl-7-hydroxy-coumarin, the condensation in presence of H_2SO_4 giving diminished yield.

Phloracetophenone on similar condensation led to a coumarin which may be either 5 : 7-dihydroxy-6-acetyl (or—8-acetyl)-4-methylcoumarin, which was also obtained when sulphuric acid was used as a condensing agent.

Gallacetophenone, quinacetophenone and *o*-hydroxy-acetophenone do not condense either in presence of aluminium chloride or sulphuric acid.

The mechanism of the formation of 5-hydroxy-coumarins is explicable on the view that the chelation between-OH and -CO.R group (R=Me or Ph) fixes the double bonds and stabilises one of the Kekule forms; the condensation takes place at the C atom joined to a C atom bearing the hydrxoyl group, by a double bond.

Section II. The condensation of simple phenols with ethyl acetoacetate.

The condensation of simple monohydric phenols with ethyl acetoacetate has been studied with aluminium chloride as a condensing agent. The condensation gives in most cases the same product as those with sulphuric acid. The yields are better by the new method, *e.g.* phenol gives 4-methylcoumarin in 30-40% yield. Phenol, three isomeric cresols and α- and β-napthols were studied. β-napthol did not give any product. The coumarins were obtained in good yield and in purer form in other cases. Their coumarin structure was established by converting them into their corresponding *o*-methoxy-cinnamic acids.

Part II. The condensation of ethyl α-aceto-glutarate with phenols.

Much work has been done on the influence of different *a*-substituents in the acetoacetic ester molecule on the course of the Pechmann and Simonis reactions. The groups mainly studied are in most cases (i) simple alkyl groups and (ii) the negative substituents like chlorine. The present investigation was undertaken with a view to (i) synthesise coumarin-3-propionic acids and (ii) to study the effect of a substituent like $-CH_2.-CH_2.-COOEt$ containing a carbethoxy group on the course of the reaction in presence of different condensing agents.

Various phenols were tried. Resorcinol, pyrogallol, α-naphthol, phloroglucinol, m- and p-cresols and orcinol condensed with the formation of coumarin derivatives. Others did not condense.

Coumarin-3-propionic acids obtained are all new. They are very stable and do not decompose though heated even above their melting points.

The results show that, compared with ethyl-α-ethyl-and α-propyl—acetoacetates, ethyl α-acetoglutarate appears to be at least as reactive, as α-ethyl acetoacetate; and more reactive than α-propyl acetoacetate. This increased reactivity may be attributed to the presence of the carbethoxy group in the alkyl chain, which probably increases the enolisation of the ester.

N. M. S.

ABSTRACTS OF M.Sc. THESES.

I—SCATTERING OF LIGHT BY WATER DROPS. BY P. B. VAIDYA.

The present work was undertaken with a view to verify Mie's theory of scattering of light in the case of large particles.

Five different sizes corresponding to $\alpha = 6, 9, 15, 20$, and 30 have been treated theoretically. The co-efficients a_n and p_n, intensity components i_1 and i_2, the total intensity i_1-i_2, and the polarization have been computed employing Mie's exact expressions. The effect of the size of the scattering particle on the intensity and polarization for various angles has been discussed.

Experimental verification has been carried out for total intensity in the case of particles corresponding to $\alpha=20$ and $\alpha=30$. The results of observations have been found to agree with the expectations of the theory within limits of experimental errors.

In the case of benzene drops the intensity has been found to rise more slowly than is found in the case of water-drops of the same size. This observation agrees qualitatively with the result obtained by Webb for alcohol drops.

AUTHOR.

II—A STUDY OF THE BEHAVIOUR OF SQUARE PLATES CLAMPED AT THEIR EDGES AND SUBJECTED TO A UNIFORM PRESSURE OVER ONE FACE. BY B. S. CHOTHIA.

(1) The solution of the problem of square plates clamped at their edges and subjected to a pressure over one face, as solved by the aid of Ritz's* method, is one which agrees with accurate experimental observations. ‡

(2) Among other things, the shape taken by an 8 cms. plate of 0.065 cm. thickness when clamped at its edges and subjected to a pressure of 10 lbs. per sq. in. over one face, is the shape shown in the Contour Map.

(3) Generally, in the case of a square plate clamped at its edges and subjected to a pressure over one face, the portion of maximum strain lies along the diameters of the plate and not along the diagonals.

(4) The shape assumed by such a plate is not materially altered by a small alteration in the pressure, but is materially altered by a small alteration in the size of the plate.

V. D. M.

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* Crelle's Journ. Bd. 135, p. 1. (1909).

‡ This method of Ritz can also be extended to the case of rectangular plates.

III—COEFFICIENTS OF VISCOSITY OF GASES. BY M. B. VAJIFDAR.

Using a modified form of Wagstaff's apparatus the following values of the coefficients of viscosities of gases have been obtained :—

For air, $\eta_{23^\circ C} = (1834.38 \pm 0.35) \times 10^{-7}$ c.g.s. units.

For Carbon dioxide, $\eta_{23^\circ C} = (1479.9 \pm 0.5) \times 10^{-7}$ c.g.s. units.

For Oxygen, $\eta_{23^\circ C} = (2038.34 \pm 0.45) \times 10^{-7}$ c.g.s. units.

For Nitrogen, $\eta_{23^\circ C} = (1767.83 \pm 0.37) \times 10^{-7}$ c.g.s. units.

The value for when substituted in Millikan's original data gave the value of the electronic charge,

$e = 4.816 \times 10^{-10}$ electrostatic units, which agrees very closely with the value of the same constant determined by X-ray methods.

AUTHOR.

IV—AN X-RAY INVESTIGATION OF THE CRYSTALS OF ORTHO- AND PARA-BENZOTOLUIDES. BY A. B. KHAN

Both crystals belong to the rhombic class (Cf. Groth, "Chemische Krystallographie" V. p. 165)

Rotation photographs gave the following dimensions of the unit cell :—

p-benzto=luide (a=26.116 A°,
b= 9.117 A°.,
c= 9.87° A°.)

o-benzto=luide (a=30.54 A°.,
b= 8.24 A°.,
c= 9.246 A°.,)

Oscillation photographs taken about the three crystallographic axes at intervals of 15° gave halvings corresponding to the space groups Q_h^{15} for the first crystal and Qh^{11} for the second.

The number of molecules calculated from the dimensions of the unit cell and the specific gravity of the crystals is eight in each case. Single molecules, therefore, form the asymmetric units of the cell.

M. R. K.

V—AN X-RAY INVESTIGATION OF THE CRYSTALS OF P-NITRANILINE, P-NITROTOLUENE, AND 1:8 DINITRONAPHTHALINE. BY R. N. MERCHANT

The single crystals were examined by rotating crystal method using copper K-radiation. The dimensions of the unit cells of the crystals are :

p-nitraniline
a=15.31 A°,
b=6 085 A°,
c=8.63 A°; β=126° 11 ;

p-nitrotoluene
a=6.41 A°,
b=14.10 A°,
c=15.39 A°

1:8 Dinitronaphthaline
a=5.39 A°,
b=14.99 A°,
c=11.35 A°

The space group and number of molecules per unit cell are given below :—

Space group	*n*	*Remarks*
p-nitraniline		
C^5_{2h}	4	Molecules asymmetric
p-nitrotoluene		
Q^5_h	8	Molecules asymmetric
1:8 Dinitronaphthaline		
Q^1_h	4	Plane of symmetry.

J. S.

VI—STUDIES IN THIXOTROPIC GELATION. BY MISS H. RATHNAMMA.

The work on the structure of gels as well as on thixotropic gelation has been reviewed and the necessity of defining "the degree of thixotropy of a gel" in terms of a measurable quantity has been pointed out. The variation with time in viscosity of thorium molybdate gel-forming mixtures which give rise to thixotropic gels has been measured. The effects on viscosity of gel-forming mixtures on (i) varying the concentrations of their constituents, (ii) adding electrolytes as well as non-electrolytes to them and (iii) changing temperature, have also been observed. It is found that the viscosity-time curves are, in all cases, not continuous and that pyridine and glycerine show a behaviour different from other non-electrolytes. Rise of temperature is found to decrease the irregular nature of the viscosity-time curves. Similar irregular curves have been obtained in the case of cerium phosphate gel-forming mixtures.

The determination of the time of set and the thixotropic time of set of thorium molybdate and cerium phosphate gel-forming mixtures shows that the former is far greater than the latter This behaviour has been explained on the view that the thixotropic time of set is the time required for the re-formation of the specific structures only while the original time of set includes the time required for the formation of micelles, for their hydration and for the formation of specific structures.

The transparency of thorium molybdate and cerium phosphate gel-forming mixtures has also been measured by an optical method using a photo-electric cell in conjunction with one stage amplification. The curves of deflection differences against time are irregular in the case of thorium molybdate but they are S-shaped and regular in the case of cerium phospate.

S. M. M.

VII—INTERACTION OF SULPHURYL CHLORIDE WITH SIMPLE AND SUBSTITUTED BENZOIC ACID AND THE ORIENTING INFLUENCES OF GROUPS IN AROMATIC ARYLAMIDE SYSTEM. BY D. R. SUKHTANKAR

Sulphuryl chloride is known to react with organic compounds as a chlorinating agent. This behaviour of sulphuryl chloride was studied in its reactions with arylamides of benzoic acid such as, anilide, o-m-p-toluidides, m-xylidide (1:3:4), p-anisidide, p-phenetidide, o-m-chloranilides, α and β - naphthylamides, o-m-p-nitranilides and the arylamides (anilide, toluidides) of p-and m-nitrobenzoic acids.

It is found that chlorine always enters the basic part of the molecule, first in the position para to the amino whenever it is free. With excess of sulphuryl chloride, wherever dichloro derivatives are obtained, the second chlorine atom is found to occupy the position ortho to the amino group, except in the case of p-phenetidide where it occupies ortho position to ethoxy.

The reaction products were identified to be, benz-p-chloranilide, benz-2:4-dichloranilide benz-3:4-dichloranilide, benz-5-chlor-o-toluidide, benz 6-chlor-m-toluidide, benz-2:6-dichlor-m-toluidide and benz-4:6-dichlor-m-toluidide, benz-3-chlor-p-toluidide, benz-3:5-dichlor-p-toluidide, benz-1:3-dimethyl-4-benzamido-5-chlor-benzene, benz-2:5-dichlor-p-anisidide, benz-2-chlor-p-phenetidide and benz-2:5-dichlor-p-phenetidide, benz-4-chlor-α-naphthylamide, benz-2:4 dichlor-α-naphthylamide, benz-1-chlor-β-naphtlyamide, benz-2-nitro-4-chloranilide, m-nitro benzanilides of p-chloraniline-5-chlor-o-toluidine, and 3-chlor-p-toluidine, and p-nitrobenzanilides of p-chloraniline, 5-chlor-o-toluidine and 3-chlor-p-toluidine.

In all the above reactions, sulphuryl chloride reacted as a chlorinating agent, and this property is made use of in further studying the orienting influences of different groups in aromatic arylamide system.

Substituted aromatic acids such as, salicylic, o-methoxybenzoic, o-toluic, and o-chlorbenzoic acids condensed with different substituted amines are made to react with sulphuryl chloride for the purpose.

In the case of salicylanilide it is observed that the p-directing influence of-OH group is greater than p-directing influence of -NHCOR, which is in turn greater than o-directing influence of -OH or -NHCOR. The same conclusion is arrived at by using different molecular proportions of the reactants. In the case of salicyl-o-toluidide, it is observed that the p-directing influence of -OH is greater than p-directing influence of -NHCOR together with -o-or-p-directing influnce of $-CH_3$. Similarly the above conclusions are fully supported by the reactions in the case of other toluidides of salicylic acid.

In the case of methoxybenzoic acid derivatives it is noticed that the p-directing influence of -NHCOR is greater than that of $-OCH_3$ group. While with o-toluic acid derivatives the order of orienting influences is as follows:

p-NHCOR > o-NHCOR > o-or-p-CH_3

Superiority of the p-directing influence of -NHCOR group over that of -Cl is observed with the reactions of o-chlorbenzoic acid derivatives.

D. R. N.

VIII—REACTIVITY OF P-ANISYLIDENE-P-METHYLACETOPHENONE. BY S. M. NADKARNI.

The chalcone was prepared by condensing together p-methyl acetophenone and p-anisaldehyde. One mol. of halogens (Cl and Br) gave with the chalcone, dihalides of the type of p-tolyl αβ-dibromo-β-p-anisylethyl ketone. Two mols. of halogens gave trihalides like p-tolyl αβ-dibromo-β-3-bromo-p-anisylethyl ketone. Potassium iodide removed α-β-halogens in the side chains giving the various chalcones. The β-halogen atoms in the side chains were replaced by alkoxy groups when the halides were heated with alcohols. These alkoxy compounds on heating gave unsaturated halides like p-tolyl-α-bromo-4-methoxy-styryl ketone which were also obtained by the action of pyridine or sodium methylate (one mol.) on the halides. Sodium methylate (two mols.), however, gave 1-3-diketones such as 3-bromo-p-anisoyl-p-tolylmethane from which the copper salts were prepared. The chalcones were condensed with ethyl acetoacetate and the resulting esters were hydrolysed. The action of potassium cyanide on some halides was also studied. A few mixed halides were prepared by the action of hydrogen bromide on alkoxy compounds and a few of their derivatives were obtained.

S. M. N.

IX—STUDIES IN THE CHEMISTRY OF DI-IMIDOCHLORIDES. BY H. K. S. RAO

The object of the present work was to prepare di-imidochlorides from diamines and to study some of their reactions. With this aim in view, the dibenzoyl derivatives of benzidine, p-and m-phenylenediamines were prepared and they gave the corresponding new di-imidochloride on heating with phosphorus pentachloride.

The imidochlorides were condensed with the following amines to give diamidines of the following formula:—

$$NRR'.CPh:N.C_6H_4.C_6H_4.N:CPh.NRR' \text{ and}$$

$$NRR'.CPh:N.C_6H_4.N:CPh.NRR'.$$

(1) o-chloraniline, (2) monomethylaniline (3) monoethylaniline (4) benzylaniline, (5) diphe-

identity of the decarboxylated product with 5-hydroxy 4-methyl 6-ethyl-coumarin (Sethna, Shah and Shah, J. C. S., 1938, 228) has been proved and hence the 8-ethyl structure as mentioned above is assigned.

The use of sulphuric acid as the condensing agent yielded the same products, but, in inferior yields.

(iii) Condensation of ethyl acetoacetate with simple polyhydric phenols.

The condensation of ethyl acetoacetate with resorcinol, orcinol, quinol, pyragallol and phloroglucinol has been studied, using aluminium chloride dissolved in dry ether or in nitrobenzene as the condensing agent. In all cases studied, the same products are obtained as with H_2SO_4 as condensing agent.

S. M. S.

XI—UTILIZATION OF WASTE PRODUCTS OF CITRUS PLANTATIONS. BY M. N. KALE.

lime (Citrus, Medica, Acida) is indigenous to India and is grown in almost all parts of the country. In Bombay Province the area under the cultivation of this fruit is 1200 acres. During the pick seasons the price of limes sometimes declines to such an extent that the growers often do not realise even the bare cost of picking, packing and transporting the fruit to the markets. Sometimes tons of limes are thrown away as a waste product in big ditches near the plantations. This investigation was, therefore, undertaken in order to find out ways and means of utilising limes for the production of marketable commodities and to work out sufficient data that would eventually enable the owners of lime plantations to put up commercial plants for the production of the same.

A preliminary investigation on a laboratory scale showed that the Bombay limes yield on an average about 53 per cent. juice and 47 per cent. of rind, seed, pulp, etc. The total acidity of the juice in terms of citric acid varied between 6. 6 and 7.0 per cent. while the citric acid content was found to vary from 6. 3 to 6. 6 per cent. The vitamin C (ascorbic acid) content of the fresh juice was about 0. 3 mg. per c. c.

Cheap limes could be utilised for the production of the following three commodities *viz.*, (i) the essential oil known as Lime oil, (ii) Lime juice to be used in beverages, (iii) Calcium citrate from the juice which is subsequently used for the production of citric acid.

Different methods for the extraction of the oil are available in the literature, out of which the distillation method was thoroughly investigated. Several experiments regarding different ways of cutting limes, separating the juice, mincing the rinds and distilling the pulp of rinds were carried out. From these experiments it was found that the yield of oil was nearly 50 per cent. more when limes were minced without the separation of juice and the pulp thus obtained distilled directly, than when the juice was first separated from limes and the juice and the pulp distilled separately. Samples of this oil were found to be marketable in the European countries. The entire economics of the process were worked out and it was found that under certain conditions the production of Lime oil will positively be a paying proposition. A Commercial plant was, therefore, designed and put into working order at a plantation in the East Khandesh District. It has successfully worked during the last three seasons. Attempts have also been made to put Calcium citrate on the market.

M. N. K.

XII—STUDIES IN COLLOIDAL SOLUTIONS. BY MR. Y. S. PARANJPE, WILSON COLLEGE, BOMBAY

Part I. Colloidal Gold : In this part simultaneous measurements of cataphoretic speed in the presence and absence of electrolytes, stability towards electrolytes and conductivity of colloidal solutions of Gold which have been dialysed, diluted, allowed to age and exposed to the cation of sun light to different extents have been presented.

It is found that with the progress of dialysis the cataphoretic speed and stability first increase, reach a maximum and then decrease, the conductivity continuously decreasing at the same time. The cataphoretic speed and conductivity of all the samples dialysed for different periods continuously decrease on diluting the sol; the stability however increases on dilution.

The cataphoretic speed generally first increases and then decreases on adding small increasing amounts of electrolytes having univalent coagulating ions, while it continuously decreases with electrolytes having bivalent coagulating ions. The idea of critical potential is not supported.

On ageing as well as on exposure to light the cataphoretic speed, conductivity and stability gradually decrease.

The results of changes in cataphoretic speed have been discussed from the point of view of changes in the adsorption of ions present in the intermicellary liquid. The physical point of view about the origin of charge on colloidal particles is supported by these results. The changes in the conductivity under different conditions are found to be largely governed by changes in the amount of electrolytes in the sol and in the number of particles per unit volume, the influence of the changes in the cataphoretic speed being relatively small.

Part II. Mutual coagulation of Prussian blue and Ferric hydroxide sols :

Mutual coagulation of Ferric hydroxide and Prussian blue sols with the progress of dialysis has been studied with reference to changes in the charge on the particles during dialysis. It is observed that with the progress of dialysis the width of the zone of mutual coagulation first decreases and then increases, the charge on the particles of the two sols first increasing and then decreasing at the same time. The results are discussed from the point of view of changes in the mutual adsorption of the oppositely charged particles of one sol by those of the other and in the amount of electrolytic impurities during dialysis.

P. M. B.

SCIENCE NOTES

A VERY SIMPLE AND INEXPENSIVE APPARATUS TO DEMONSTRATE THE PRINCIPLES OF TELEVISION.

By

PROF. R. V. BARAVE, M.SC.,
Willingdon College, Sangli.

The accompanying diagram shows a very simple type of arrangement that is quite convenient to explain the underlying ideas of a general scheme of television.

Two scanning discs D_1 and D_2 are run on a single shaft rotated by an electric motor. Light from a carbon arc is passed through a condenser and falls on the disc D_1. A stencil S of a simple diagram or a letter serves as an object and its real image is formed by the lens L on the photo-cell P. The disc D_1 scans the objects and the pulses generated are amplified by a two stage $r-c$ coupled amplifier. The output of the amplifier directly feeds the neon-lamp L which is properly biassed. The lamp is kept behind the other disc D_2. The observer can see the stencil image reproduced in the neon-red colour. Thus,

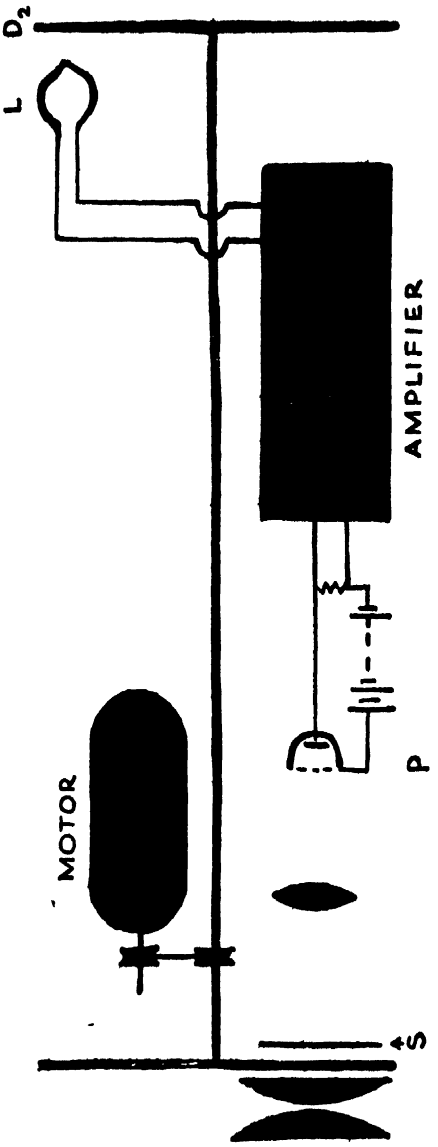
(1) The idea of scanning can be very easily explained.

(2) By holding glass pieces of different transparency in the position of the object, the variation of the intensity of the neon-glow with the intensity of the incident light can be conveniently shown.

(3) By slightly displacing the disc D_2 with respect to D_1 the importance of sychronization as distinct from isochronism of the disc can be demonstrated, etc.

Considering the highly complicated and technical nature of the subject of television, the inexpensive simplicity of the apparatus is the main point of interest.

The work was carried out in the Fergusson College, Poona and considerable help was received from Mr. K. R. Karve an old student.


D_2
L
AMPLIFIER
P
MOTOR
S

NOTES AND NEWS

The world is passing through most momentous times. It was on the brink of a great war only very recently. The war was averted somehow or other for the time being but it is doubtful whether it has brought in an era of peace. The peace sought for was not the result of a spontaneous desire for the same from *within* on the part of everybody concerned; it appears to have been brought about by a pressure from *without*; hence it cannot be a lasting peace. This is evident from the fact that there is still a race of armaments going on, perhaps more vigorously than before. In the survey recently made by the military experts of the United States of America it was reported that the standing armies and reserves of the big powers totalled about fifty five million men and the estimated expenditure on them for the year 1937 came to a figure somewhere between 2500 and 3000 million pounds. What an enormous expenditure! What a crushing burden to the taxpayer! Could not these vast regiments of men be better employed than for purposes of destruction? How long will such a state of affairs continue?

To solve this complicated problem Dr. Bhagavan Das of Benares, an ex-member of the Indian Legislative Assembly, suggests in his brilliant and thought-provoking article[1] entitled "The World's Dire Need for a Scientist Manifesto" that the scientists, philosophers, thinkers and University Professors of the world should unite, meet in a conference, put their heads together, and evolve a scheme of "Social Structure" in accordance with the "Law of Alliance for Existence" and in which Evolution by the law of the "Struggle for Existence" should take a subordinate place. "The Universities", he writes, "should supply *spiritual bread* directly to all *mankind*, and should point out to all, the practical way in which a sufficiency of *material* bread can be supplied to each person. Commenting on this article the Editor, *Nature*,[2] rightly observes "Peradventure where politicians have failed men of science may find a way of approach to disarmament, military and economic."

Dr. Bhagavan Das makes a wise observation in his article when he says "Science is for life, not life for Science. That life, mind, consciousness is more and other and greater than *matter*; that the divorce of science from humanist morality and spirituality is one cause of the present horrible condition of the mutual relations of the nations, and of the classes or sections within each nation." For the solution of the knotty problems of war, unemployment and poverty facing humanity, mind control alone is not enough; a *controlled* mind without it being at the same time a *purified* mind would be a danger to society, as a glance at the present-day events will show. What is wanted is a combination of both. We commend this article to our readers.

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[1] The Indian Theosophist, March 1938.
The Theosophist, April 1938.

[2] Nature, August 6, 1938, p. 247.

DR. T. S. WHEELER.

We regret to record the news of the departure, on 22nd October, of Dr. T. S. Wheeler on leave preparatory to retirement. Dr. Wheeler came to India in 1931 as Principal and Professor of Organic Chemistry of the Royal Institute of Science, Bombay. Before he came to the Institute he had a brilliant record as a student at the Royal College of Science, Dublin, and at the University of London, and as a member of the staff of the Royal Naval Cordite Factory, Research Department of Royal Arsenal, Woolwich, and the Imperial Chemical Industries, Ltd., and had published 40 papers and had taken 20 patents.

During his short tenure of office Dr. Wheeler proved himself to be an able administrator and a keen researcher and devoted all his time and energy in making the Institute an active centre of scientific research. It is remarkable to find that during the last seven years nearly 110 students took the M.Sc. degree of the Bombay University from the Institute and about 280 original papers were published in various Journals in India and abroad. Out of these he himself and along with his students published about 56 papers on organic and physico-organic subjects. One of the most important contributions by him is a modification of a method of synthesis which was given up as impossible forty years ago, in such a way that the desired products (flavones) could be easily obtained with certainty. He also synthesised a number of naturally occurring substances by methods of his own in a simple and easy manner. He successfully studied the long standing problem of the benzoin reaction and worked out a theory of the liquid state of matter which has now come to be associated with his name.

Dr. T. S. WHEELER

Ph.D , D Sc., F.R.C.Sc., F.I.C , F Inst P.,
A.M.I.Chem.E., F N.I., J.P.

Equally great and important was the contribution of Dr. Wheeler towards the activities of the University of Bombay which shows how interested he had been in promoting the general education of the Bombay Presidency. The University had been contemplating for long, as a matter of fact several schemes were mooted, for the establishment of a University Department of Chemical Technology but it is no exaggeration to mention that the actual practical scheme was suggested by Dr. Wheeler who also worked out all the preliminary details for the equipment of the Department. Even after the Department had started functioning he was every now and then consulted on all important matters concerning the department and his suggestions were always found to be very useful. Dr. Wheeler also took a very active part in various other committees of the University and contributed largely towards strengthening the courses and raising the standard of examinations.

Dr. Wheeler's worth as a scientific worker can be seen from the high position he occupied in the various scientific associations in India. He was the Vice-President of the National Institute of Sciences of India, the Indian Academy of Science, Bangalore, and the Institution of Chemists, India, and a member of the Editorial Board of the Indian Chemical Society, Current Science and the Journal of the University of Bombay. His last scientific activity was the recent meeting of the National Institute of Sciences of India, in Bombay, at which interesting papers were read and discussed on the synthesis of naturally occurring products by prominent workers in India.

Dr. Wheeler has great social qualities and had collected a large circle of friends and admirers. He is kind at heart and has a very charitable disposition. By his departure the Institute and the University lose an active scientific worker and an admirable guide. We are glad to learn that he has been offered an appointment as State Chemist to the Government of Eire, which he is taking up next year.

M. P.

PROFESSOR R. B. FORSTER

Sir James Irvine, F.R.S, who had come out to India in 1936 as Chairman of the Indian Institute of Science Reviewing Committee, stated in a press interview in Bombay before he left for Europe that he had formed a very high opinion of the new

Department of Chemical Technology of the Bombay University; it was extremely well equipped, the standard of education was excellent, and it was conducted by several enthusiasts (*Chemistry and Industry*, May 8, 1936, p. 385). The unique position occupied by the Department in the Universities and among Technological Institutes in this country, and the fact that the Department bears very favourable comparison with similar institutions in the west, are now admitted on all hands. It is perhaps not so widely recognised, particularly among those responsible for the administration of Indian Universities, that the Department has been organized and equipped with the utmost economy of expenditure in comparison with the results accomplished and with the outlay on technological departments in Europe or America. The bulk of the credit for this achievement is due to Professor R. B. Forster, A.R.C.Sc.I., Ph.D., D.Sc., F.I.C., who has just relinquished the post of Mody Professor and Head of the Department of Chemical Technology. With his unusual training as a chemist and an engineer, his versatility and his wide experience, he has brought to his task a combination of qualities without which the organization of the Department in its present form would not have been possible. The present writer has some knowledge of the occupants of Chairs of Chemical Technology in the United Kingdom and he has no hesitation in congratulating the University of Bombay on its choice of the first Head of its Department of Chemical Technology; no one else in India or Great Britain could have carried to completion the first stage of this great undertaking with such signal success.

Professor Forster's university education was commenced in the Royal College of Science, Dublin, where he graduated with the A.R.C.Sc.I. in applied physics in 1900 and with the same degree in applied chemistry a few years later. From 1908 to 1911 Dr. Forster carried out research in the University of Berlin in chemistry and chemical technology, obtaining the degree of Ph.D. in 1911. After five years of further research he was awarded the D.Sc. by the National University of Ireland in 1916 and the Fellowship of the Institute of Chemistry in 1919. The remarkable feature of Dr. Forster's technological training is his varied works experience, first in the English Electric Co., Preston, then in the Canadian General Electric Company, Peterboro, Canada, the Western Electric Co, Chicago, and for five years as a research and factory chemist and later as a *liaison* officer attached to the production and control Department in Messrs. Levinstein Limited, which is now part of the Imperial Chemical Industries (Dyestuffs

Group). As a teacher, Professor Forster began in the Kingstown and Blackrock Municipal Technical Schools as an assistant lecturer in Physics and Chemistry. For five years between 1911 and 1916 he lectured to graduates in chemistry in the University College, Galway (National University of Ireland) and in 1921 he proceeded from Levinsteins to the University of Leeds where he continued to be the Senior Lecturer in the Department of Colour Chemistry and Dyeing, until he was appointed in 1933 by the University of Bombay as the first Professor of Chemical Technology and Head of the Department, and was entrusted with the whole work of elaborating the plans, ordering out the machinery, erecting the plant and organising the new Department with regard to every detail of its many sided activities.

Professor Forster arrived in Bombay on the 26th October, 1933, and set out immediately to complete the plans for the necessary structural alterations in the East Wing of the Royal Institute of Science Building. Consisting as it does of large halls and rooms of irregular shape, it was singularly unsuitable for the purpose of a technological Department, and it needed all the skill and initiative of Professor Forster to provide for the machine equipment, laboratory benches, etc., of the various sections of the Department. The first consignment of textile machinery from England arrived in July 1934 and scarcely a month after the first batch of students was admitted. The work of erection and equipment had to proceed, therefore, simultaneouely with the work of laying down the syllabuses and of organising the lecture work and practical classes. Space does not permit of enlarging further on the numerous duties which Professor Forster had to perform in the early stages of the development of the Department and of the many difficulties he had to overcome. Since the Department in its present state, the courses of study organised and the facilities for industrial research which are available, are adequately described in the prospectus of the Department, it need only be added that the Department has already been brought to the highest level of efficiency possible in the very limited space which has been allotted to it.

During the brief period of its existence the Department has had an excellent record of work. The three batches of graduates in Textile Chemistry and Chemical Engineering have all been absorbed by industry or are carrying out research for higher degree in Chemical Technology in the Department or elsewhere. While the primary function of the Department to impart advanced training in Textile Chemistry and Chemical Engineering to graduates in chemistry to enable them to occupy responsible positions in industry is being satisfactorily fulfilled, the Department has also been available to the industries of the Province as a central research and analytical laboratory. In the case of the cotton mills the Department serves as a Test House in which the dyes, chemicals and auxiliary agents used by the processer are submitted to chemical examination and practical trials. Research of a more fundamental character on cellulose, dyestuffs and textile auxiliaries and on processing problems has also been in progress and a series of important papers in well known journals, such as the Journal of the Society of Chemical Industry and the Journal of the Society of Dyers and Colourists, have already issued from the Department.

The Department of Chemical Technology will stand as a permenent memorial to Professor Forster. In his recent Convocation Address the Vice-Chancellor expressed his appreciation of the very valuable services rendered to the University by Professor Forster and of the sincerity and devotion to duty which have characterised his work from the time he was placed in charge of the Department. The University may be assured of Professor Forster's continued interest in the Department; the best tribute to his pioneering work would be to move the Department to a more spacious, suitable and worthy location and to endow it on a scale that would enable it to go from strength to strength and to be for all time the premier College of Technology in this country.

K. V.

PROFESSOR KOLHATKAR'S JUBILEE

We are very glad to congratulate Professor G. B. Kolhatkar on the completion of his 60 years. He is one of the most senior teachers of Chemistry in the Bombay Presidency and has taught chemistry to a very large number of students.

He was born on 1st September 1878 in a small village in the Satara District. His education was taken in his village and later in Bombay. He passed the B.A. in 1904 getting half the Narayen Vasudev Scholarship and the M.A. in 1906 winning the Chancellor's Medal. After working for some time in the Aryan Education Society's School and in Professor Gajjar's Techno-Chemical Laboratory, he joined the Fergusson College in 1907, where he is working as the head of the Chemistry Department for the last 30 years. He was one of the first students in the Indian Institute of Science at Bangalore. Besides doing undergraduate teaching, he has devoted some time to the investigation of the hydrolysis and alcoholysis of various esters and ethers and has published some papers in research Journals.

Professor Kolhatkar has been a member of the University Senate, the Faculty of Science and the Board of Studies in Chemistry for over 15 years. He has been twice Dean of the Faculty of Science and for a number of years a member of the Academic Council. His work in the University, though unostentatious, has been appreciated by all who came in contact with him.

Professor Kolhatkar's students and admirers met in Poona on the 3rd of September last and presented an address to him on the occasion of his jubilee. A fund to commemorate the event was also collected and handed over to the Fergusson College for awarding two prizes for graduate and post-graduate students of Chemistry of the College. We wish Professor Kolhatkar a long and healthy life of work and prosperity.

D. D. K.
(Poona).

OBITUARY

The Late Mr. N. W. Hirwe, B.A., M.Sc., A.I.C.

Narhar Waman Hirwe died in Bombay on 11th August, 1938, following an operation. Born in 1898, he was educated at New English School, Poona, and Fergusson College, Poona, from where he passed the B.A. and the B.Sc. examinations of the Bombay University in 1921 and 1923, respectively. In June, 1923, he joined the Royal Institute of Science, Bombay, to carry out research work under the guidance of the late Dr. A. N. Meldrum. Here he was elected a Fellow during 1924-1925, and worked hard to complete his work for the M.Sc. degree of the Bombay University which he took with Distinction in 1926, on the submission of a thesis entitled, 'Nitrosalicylic acids.' In June 1926 he joined the chemical staff of the Wilson College, Bombay. In 1929 he joined the staff of the Royal Institute of Science, where he continued to work uptil his death. He was a recognised postgraduate teacher of the Bombay University and was elected an Associate of the Institute of Chemistry, Great Britain and Ireland, in November, 1937.

At the Institute Mr. Hirwe soon made a mark as a keen research worker and undertook to guide the researches of students working for the M.Sc. degree. Seven students took their degree on the basis of the work carried out under his guidance. The list of his publications attached herewith will show that he was chiefly interested in salicylic acids and chloral condensation.

He leaves behind him his widow, four children and a large number of friends and admirers to mourn the loss.

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7	Derivatives of salicylic acid, Part VIII. Interaction of thionyl chloride with esters of hydroxy aromatic acids, in the presence of finely divided copper. Part III.	J. Ind. Chem. Soc., 1934, 11, 551-554.
8	Derivatives of salicylic acid, Part VI. Interaction of thionyl chloride with esters of hydroxy benzoic acids in the presence of finely divided copper, Part I.	J. Amer. Chem. Soc., 1935, 57, 101-103.
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13	Derivatives of salicylic acid, Part XII, Nitro-salicylic acid and their methylethers.	Proc. Ind. Acad. Sci., 1937, V, 377-379.
14	Derivatives of salicylic acid, Part XI, Bromosalicylic acid and their methyl ethers.	Proc. Ind. Acad. Sci., 1937, V, 321-25.
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M. P.

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EXTERNAL STRUCTURES OF THE DESERT LOCUST

(*Schistocerca gregaria*, Forsk.)

(With 52 text-figures)

BY

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INTRODUCTORY REMARKS.

The desert locust which is entomologically included in the family Acrididæ, is ecologically a tropical pest, having migratory habits. It has a very wide range of distribution that extends from Morocco in the North-West Africa, right through Egypt, Sudan, East Africa, Arabia, Persia, Baluchistan to Sind, the Punjab and Central India. The locust has two phases: the solitary and the migratory. The *solitary* phase is usually found, though in sparse numbers, in the semi-desert areas within the range of its distribution noted above. Under favourable conditions of temperature and rainfall, the solitary phase of the locust multiplies enormously, and gives rise to what is commonly known as the *migratory* phase. Large swarms are formed which, instead of remaining localised in their initial breeding areas, migrate from place to place, gaining strength from other breeding areas on their way, and destroying whatever green crosses their path. Knowledge regarding the direction and motive of these migratory flights is still in its infancy, although several hypothetical explanations have been advanced to explain the mysterious phenomenon. The damage done by this pest in its migratory phase is indeed incalculable, the more so since it is an international pest with extensive distribution over the continents of Africa and Asia. But the fact that the various countries including India, which periodically suffer from its deadly ravages, have started special Investigation Bureaus to study the bionomics of this pest, would easily testify to its economic importance, both from the Agricultural and Entomological points of view.

In spite of the unique importance of this pest and the wide interest it has lately created in several countries, no work of any exhaustive nature seems to have been done so far on the *external morphology* of this locust. Finding this dearth of a good morphological description, the writer, during his stay in England in the summer of 1930, undertook to study the external structures of this insect, on the advice of Mr. B. P. Uvarov of the Imperial Institute of Entomology, London. Dried and preserved material of the desert locust was made available to the writer by Dr. C. B. Williams, the then Lecturer in the Entomology Department of the University of Edinburgh. The studies included in this paper, dealing with the external morphology of the desert locust, were all carried out, both text and drawings, in the Entomological Laboratory of the Edinburgh University, during the winter of 1930–31, under the general supervision of Dr. C. B. Williams.

The writer takes this opportunity to express his gratefulness to Mr. B. P. Uvarov and to Dr. C. B. Williams, for suggesting the problem and supplying the material and other facilities respectively. The writer is also grateful to Prof. P. R. Awati, Royal Institute of Science, Bombay, for help and encouragement, regarding the publication of this paper, in the *Journal* of the Bombay University.

HEAD–CAPSULE

The head-capsule of *Schistocera gregaria* (Figs. 1, 2), which forms the anterior portion of the body, occupies a somewhat vertical position in front of the thoracic region and has the mouthparts hanging downwards. The mid-dorsal region of the head-capsule, situated between and behind the *compound eyes* (E), is known as the *epicranium* (EP) which carries a median longitudinal suture, the *epicranial suture* (EPS), also known as *coronal suture* (Snodgrass, 1928). Anteriorly the epicranial suture divides into two branches called the *frontal sutures* (FS) which run towards and along the dorso-mesial margins of the compound eyes. The area in front of the frontal sutures is called the *frons*, while the mid-dorsal point of junction, situated between the compound eyes, is usually known as the *vertex* (V). The posterior portion of the epicranium, adjoining the "foramen magnum," is called the *occiput* (OC) to which is also attached a small *post-occipital area* (POC).

The *frons* is limited dorsally by the frontal sutures (FS), ventrally by the fronto-clypeal or *epistomal suture* (FCS), and laterally by the compound eyes (E) and the *fronto-genal sutures* (FGS). The most prominent feature of the frons is the presence of a median, elongated, raised area called the *frontal costa* (FC) which is bordered laterally by a strong ridge on each side, the *frontal carina* (CR). On either side of the frontal costa, between it and the compound eye, is situated a cavity or socket into which is planted the *antenna* (AN). Ventral in level to the antennal socket lies the *sub-antennal suture* (SAS), curved in outline. Lateral to the antennal socket, between it and the compound eye,

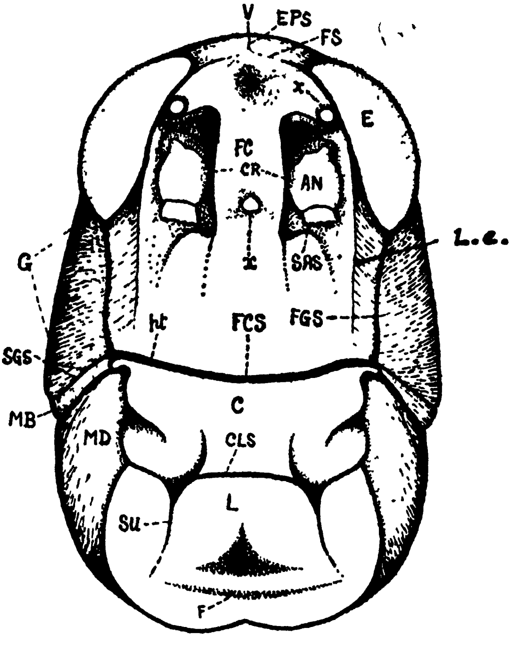


FIG. 1. Front view of the *head*. × 6.

AN—Antenna. C—Clypeus. CLS—Clypeolabral suture. CR—Frontal carina. E—Compound eye. EPS—Epicranial suture. FC—Frontal costa. FCS—Fronto-clypeal suture. FGS—Fronto-genal suture. FS—Frontal suture. G—Gena. L—Labrum. MB—Mandibularia. MD—Mandible. pt—Pit. SAS—Subantennal suture. SGS—Subgenal suture. SU—Suture. V—Vertex. X—Ocellus. Le.

is seen a conspicuous ridge, the *lateral carina* (LC), which runs straight towards the fronto-clypeal suture, becoming obscure distally. Besides the two large compound eyes (E), three small ocelli (×) are present, two of which are situated in the dorso-lateral corners of the frontal costa, while the third one is located in a shallow median depression on the costa itself, a little above the level of the sub-antennal sutures.

The *antennæ* (Figs. 1, 3. AN) are situated in deeply sunken areas, one on each side of the frontal costa (FC), between the latter and the compound eye (E). Each antenna is lodged in a membranous circular area (ANC) (*Antacorium*, Yuasa, 1920), surrounded by a deeply chitinised ring, the *antennal sclerite* (ANSL). The *scape* (SC) which forms the first antennal segment is a strongly built piece, and measures 1·56 mm. in length and 1·4 mm. in breadth (♀). It carries a few hairs and sensory papillæ

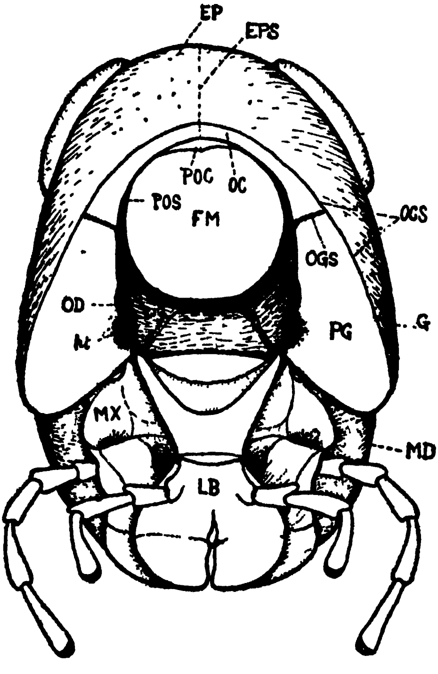


FIG. 2. Back view of the *head*. ×5.

E—Compound eye. EP—Epicranium. EPS—Epicranial suture. FM—Foramen magnum. G—Gena. LB—Labium. MD—Mandible. MX—Maxilla. OC—Occiput. OCS—Occipital suture. OD—Odontoidea. OGS—Occipito-postgenal suture. pt—Pit. PG—Postgena. POC—Post-occiput. POS—Post-occipital suture.

along the dorsal side of its body. The scape is articulated to the rim of the antennal socket at two points, latero-ventral and mesial. The latero-ventral articulation (LV) consists of a basal process of the scape (*Antartis*, Yuasa, 1920) hinged movably with a notch in the latero-ventral corner of the rim of the antennal sclerite. The mesial articulation (MA) is formed by the mesial side of the base of the scape, being joined to the rim of the antennal sclerite by means of an elastic chitinous ligament. Between the basal margin of the scape and the antennal rim lies an extensive membrane, the *antacorium* (ANC) which is capable of deep flection, and which thus facilitates a dorso-ventral movement of the scape between the two lateral and mesial articulatory points. The muscles regulating this movement are attached to two apodemes arising from the base of the scape in its ventral and dorso-lateral corners. The *pedicel* (PD) which forms the second segment of the antenna is almost as broad as long (length–0.45 mm., breadth–0.5 mm. (♀)). It carries a dicondylic type of articulation to the scape, the points of attachment being so located as to effect the movement of the pedicel almost in a horizontal plane. The pedicel is followed by a long *flagellum* composed of 25 similarly formed segments which are all immovably joined to each other.

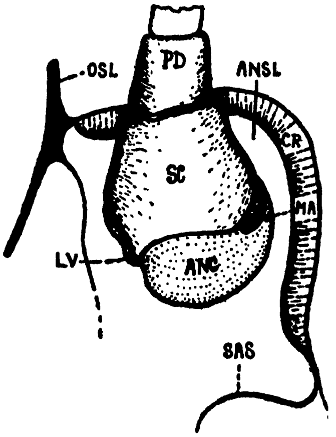


FIG. 3. *Antennal base.* ×20.

ANC—Antacoria. ANSL—Antennal sclerite. CR—Frontal carina. LV—Latero-ventral articulation. MA—Mesial articulation. OSL—Ocular sclerite. PD—Pedicel. SAS—Subantennal suture.

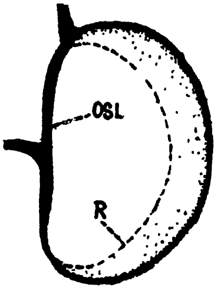


FIG. 4. *Ocular sclerite* showing the internal posterior rim. ×8.

OSL—Ocular sclerite. R—Rim.

The area on each side of the epicranial suture is named by Crampton (1921) as the *parietal region*. In the antero-lateral corners of the parietal region are situated the large oval *compound eyes* (E). Each eye is surrounded by a chitinous ring called the *ocular sclerite* (Figs. 3, 4. OSL), *oculata* (Yuasa, 1920). Its posterior margin extends in the form of a rim (R) within the ocular cavity. In the dorsal corner of the compound eye is seen a small oval spot which is easily distinguishable from the remaining portion by its transparent clear surface.

The lateral area below the compound eye on each side is called the *gena* (Figs. 1, 2. G) which is limited anteriorly by the fronto-genal suture (FGS), ventrally by the subgenal margin (SGS) and posteriorly by the *occipital suture* (OCS). The region posterior to the occipital suture is deflected at right angles towards the *foramen magnum* (FM). It is distinguishable into a narrow strip, the *occiput* (OC) and a broad ventral area, the *postgena* (PG).

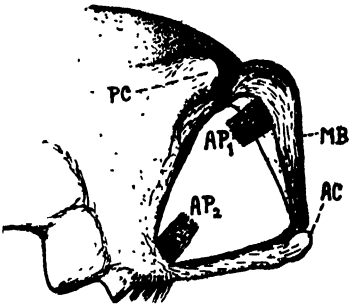


FIG. 5. *Mandible* showing the triangular base. ×15.

AC—Anterior mandibular condyle. AP_1, AP_2—Apodemes. MB—Mandibularia. PC—Posterior mandibular condyle.

Between them runs a short transverse suture (OGS). The latter is usually found to be obsolete in other locusts and grasshoppers (Snodgrass, 1928), but in *S. gregaria* it is distinctly seen. Posterior to the occiput is a small median sclerite, *the post-occiput* (POC), separated from the occiput and postgena by the *post-occipital suture* (POS). The latter extends ventrally and sets off a strongly developed band-like rim (post-occipital rim) which forms the margin of the foramen magnum, and to which is attached the neck-membrane. At the ventral extremity of this suture on each side is situated a widely open *pit* (pt) which leads within into the posterior tentorial arm of the tentorium on either side. Just a little dorsal to these post-tentorial pits, the post-occipital rim develops on each side a rounded elevation (OD) (*odontoidprocess*, Yuasa 1920; *occipital condyle*, Crampton, 1921) with which articulates the lateral cervical sclerite from the neck-region described further on.

In regard to the *homology* of the occipital suture, Snodgrass (1928) suggests that the suture may be intersegmental in origin separating the mandibular from the maxillary segment of the primary insect-head. Regarding the post-occipital suture the same author is inclined to support the view that the suture in question represents the intersegmental groove between the maxillary and labial segments. Internally the suture forms a ridge, the post-occipital ridge, which according to Imms (1931) "appears to be a true intersegmental phragma between the maxillary and labial segment." The post-occipital sclerite would thus constitute the remnant of the labial segment (second maxilla).

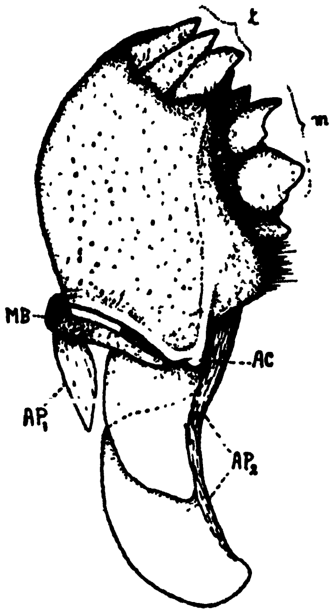


FIG. 6. *Left mandible.* ×8.

AC—Anterior articulatory process or condyle. AP—Apodeme. MB—Mandibularia. m—Molar teeth. t—Incisor teeth.

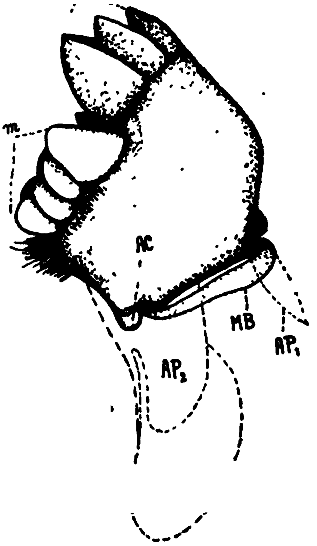


Fig. 7. *Right mandible.* ×8.

Lettering as in Fig. 6.

MOUTH PARTS

The mouth parts of *S. gregaria* consist of the clypeo-labrum in front, a pair of mandibles and maxillæ at the sides, and the labium behind.

CLYPEO-LABRUM :—The *clypeo-labrum* (Fig. 1. C-L) occupies the anterior area of the mouth region, and is somewhat convex on its external surface. The two parts, *clypeus* (C) and *labrum* (L), are joined to one another by means of the *clypeo-labral suture* (CLS) which allows the labrum to move slightly backward and forward. Dorsally the clypeus is connected with the frons (F) along the epistomal suture (FCS) which laterally carries the *pits* (pt) of the anterior tentorial arms (Fig. 19. AT). The dorso-lateral corners of the clypeus are produced into small curved lobes, and in the notches thus formed (Figs. 8, 14. n) are inserted the anterior condyles of the mandibles of either side (Fig. 8. AC). The lateral margins of the clypeus show suture-like clefts which extend mesially to a short distance and represent an incomplete clypeal suture dividing the clypeus into the *pre-clypeus* and the *post-clypeus* (Yuasa, 1920).

The *labrum* (L) is a broad suboval plate, having its ventral margin medially notched and corners rounded. On its slightly convex surface are seen a few sutures and furrows. Two of them (SU) are somewhat conspicuous and branch off ventralwards from the transversely situated clypeo-labral suture. Towards the ventral margin of the labrum these sutures are joined to one another by a transverse furrow (F). Within the square thus enclosed is seen a small T-shaped depression or groove with its arms running parallel to the ventral transverse furrow. The

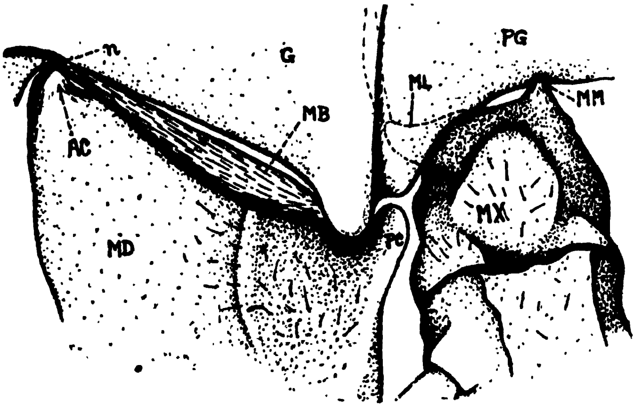


FIG. 8. Basal regions of *mandible* and *maxilla* showing their respective articulations with the ventral margin of the head-capsule. ×15.

AC—Anterior mandibular condyle. G—Gena. MB—Mandibularia. MD—Mandible. ML—Lateral articulatory process of maxilla. MM—Mesial articulatory process of maxilla. MX—Maxilla. n—notch. PC—Posterior articulatory process of mandible. PG—Postgena.

clypeo-labral suture gives rise to a strong internal ridge which sends out from its lateral corners chitinised processes known as *tormae* (Fig. 14. TM). Each torma extends mesially inwards and sends up a dorsally running tendon for muscle-attachment.

MANDIBLES :—The *mandibles* (Fig. 1. MD) are situated one on either side of the clypeo-labrum. Each mandible has a triangular base (Fig. 5), is convex on the outer surface (Figs. 6, 7.), and carries a strongly chitinised dentate distal margin. It is articulated to the ventral border of the gena, along the outer side of its triangular base at two points, the anterior and the posterior (Fig. 8). The anterior articulatory point consists of the mandibular process (AC) which fits into the socket or notch (n) formed in the dorso-lateral corner of the clypeus (*vide supra*). The posterior articulatory point is situated in the postero-lateral angle of the mandibular base, which is produced into a process (PC) that interlocks with a similar process from the ventral margin of the gena. Between these articulatory points intervenes a thinly chitinised membranous strip known as *mandibularia* (MB) (Yuasa, 1920), which joins the mandibular base with the ventral genal margin. In the vicinity of the posterior articulation of the mandible, the mandibularia gives off internally an apodeme for muscle-attachment (Figs. 5, 6. AP_1). The other two sides of the triangular base of the mandible which are invisible from outside, project within the preoral cavity and remain attached to the membranous sides of the hypopharyngeal region (Figs. 5, 15). From the innermost corner of the mandibular base is given off within the "cranial cavity" a strongly chitinised apodeme

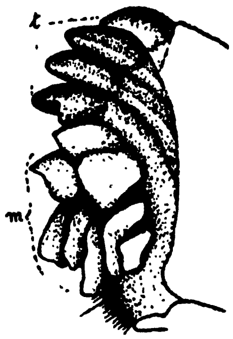


FIG. 9. *Teeth* region of the *left* mandible. ×8.

m—Molar teeth. t—Incisor teeth.

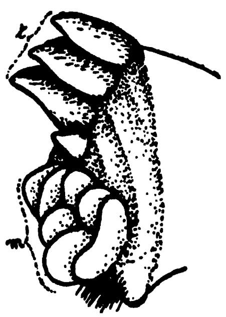


FIG. 10. *Teeth* region of *right* mandible. ×8.

m—Molar teeth. t—Incisor teeth.

(Figs. 5, 6, 7. AP_2) which is folded leaf-like and serves for muscle-attachment.

The distal margin of the mandible carries a number of strongly chitinised *teeth* (Figs. 6, 7, 9, 10) which can be distinguished into the grinding *molars* (m) and the cutting *incisors* (t). The incisors which project from the distal apical region of the mandible are strongly developed, pointed, curved teeth. Proximal to them on the mesial side of the mandible are situated the molars with broad bases and rounded apices. The numerical strength and deposition of the incisors and molars show variations in the right and left mandibles of the same specimen (Figs. 9, 10). The left mandible (Fig. 9) carries four incisors in addition to a small dentate process arising from the proximal one. They have all sharply pointed apices. The right mandible (Fig. 10) also carries four incisors of which the distal three are large and the proximal fourth small. The apices of these are irregularly pointed. The molars, which are placed somewhat obliquely, in the inner proximal region of the mandible, count seven in the right and eight in the left mandible. The molars of the right mandible occupy a smaller area and have rounded apices, while those of the left mandible occupy a wider area and have slightly conical apices. Moreover the deposition of the molars is just the opposite in the right and left mandibles. The molar teeth of the right mandible are crowded more towards the inner basal region. Those of the left mandible are crowded more towards the outer margin. This asymmetrical arrangement of the molar teeth presumably facilitates their working against each other when the mandibles are in action. Along the base of the molar region is situated a bunch of hairs which are directed towards the oral opening. They are presumably useful, as is pointed out by Snodgrass (1928), in preventing the escape of masticated food material from between the jaws. In addition to the asymmetrical arrangement of the mandibular teeth noted above, the right and left mandibles show variation in their size. The left mandible is found to be a little bigger than the right one.

MAXILLÆ :—Posterior in position to the mandibles are situated the *maxillæ* (Fig. 2. MX), one on each side of the medially placed labium (LB). Each maxilla is articulated to the ventral margin of the postgena at two points (Fig. 8). The basal region of the maxilla sends out a pair of processes, anterior and posterior, which work against a pair of corresponding grooves in the post-genal margin, one process (ML) being fitted along the inner side and the other (MM) along the outer side of the ventral margin of the post-gena.

Each *maxilla* (Fig. 11) is composed of three principal divisions: *cardo*, *stipes* and *palpifer* (Crampton, 1928). Of these the stipes is provided with an endite, the *lacinia*, and the palpifer with a similar endite, the *galea*. The cardo is further divided into a main portion, the *vera-cardo* (CV), and a narrow strip along its inner side, the *juxta-cardo* (CJ). The vera-cardo which from its base sends off the two articulatory processes (MM, ML), has a convex outer surface. Distally it is joined to the stipes by means of a suture with a strong internal ridge. Nearer its distal margin the vera-cardo carries a deep *pit* (pt) on its surface which internally gives rise to a blind chitinous apodeme for muscle-attachment.

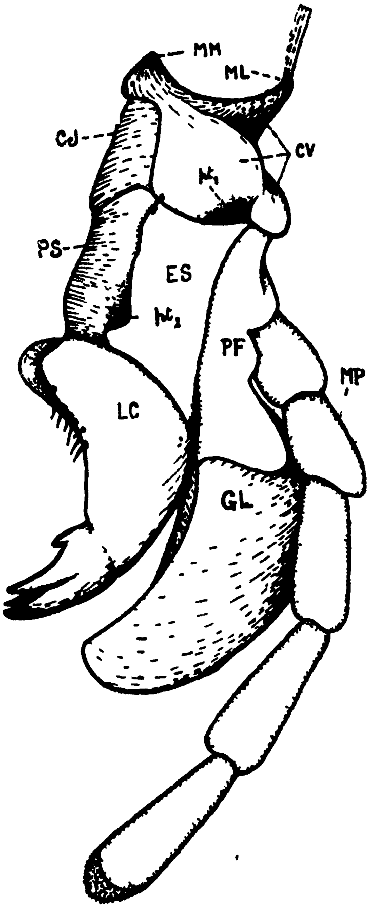


FIG. 11. *Maxilla.* ×15.

CJ—Juxta-cardo. V—Vera-cardo. ES—Eustipes. GL—Galea. LC—Lacinia. MM, ML—See Fig. 8. MP—Maxillary palp. PF—Palpifer. PS—Parastipes. pt—Pits.

The *stipes* which is somewhat subquadrate in form, is secondarily divisible into a narrow *para-stipes* (PS) and a rectangular *eustipes* (ES) (Crampton, 1925). The parastipes forms the oblique, inner face of the stipes. To the distal margin of the stipes is attached its endite, the *lacinia* (LC), which has a broad base and a narrow curved distal end. It is convex on its outer side and concave on its inner face. It terminates in three strongly chitinised teeth which are curved inwards. On its inner proximal margin it carries a few stiff hairs directed towards the preoral cavity. From the mesio-dorsal corner of the lacinia is given off internally a muscle-apodeme which regulates its movement in the transverse plane.

The *palpifer* (PF) is a narrow thinly chitinised area, demarked from the eustipes by means of a lateral suture. Laterally it gives off the *maxillary palp* (MP), and distally, its endite–the *galea* (GL). The maxillary palp is five-segmented, the last segment being the longest. The latter has a rounded tip which carries a number of small sensory setæ having a gustatory function (Crampton, 1916). The galea has the form of a flattened lobe with a convex outer surface. On its inner side is seen an incomplete suture, apparently dividing the galea into two portions.

LABIUM:—The *labium* (Figs. 2, 12. LB) or the lower lip is

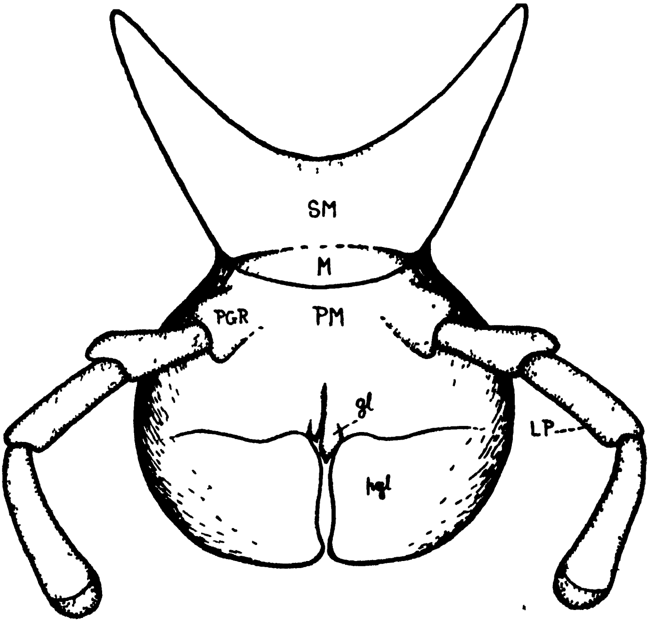


FIG. 12. *Labium.* ×15.

gl—Glossa. LP—Labial palp. M—Mentum. pgl—Paraglossa. PGR—Palpiger. PM—Prementum. SM—Submentum.

situated between the two maxillæ, and forms the posterior appendage of the mouth parts. It is movably attached to the head-capsule in the ventro-mesial corners of the post-gena (Fig. 2), a little ventral to the external *pits* (pt) of the posterior tentorial arms. The labium is formed of the submentum (SM), mentum (M), prementum (PM), palpiger (PGR), glossæ (gl), and paraglossæ (pgl).

The *submentum* (SM) is a large plate having a broadly crescentic dorsal margin held between the widely produced dorso-lateral arms by which it is attached to the ventro-mesial corners of the post-gena. Ventrally it gradually narrows down to form a constricted neck which marks its connection with the distal premental region. The *mentum* (M) which is very much reduced in this locust, is confined to a small narrow transverse strip situated between the submentum and the prementum along the constricted neck region mentioned above. The *prementum* (PM) is quite a broad plate carrying distally two pairs of appendages, one pair of small medians, the glossæ (gl), and the other of large laterals, the paraglossæ (pgl). The *glossae* are unequal in size, the right lobe being larger than the left one. Besides, they are asymmetrically placed, the right one more or less occupying a median position. The *paraglossae* (pgl) have a flattened plate-like form, and are somewhat convex on their outer surface. The

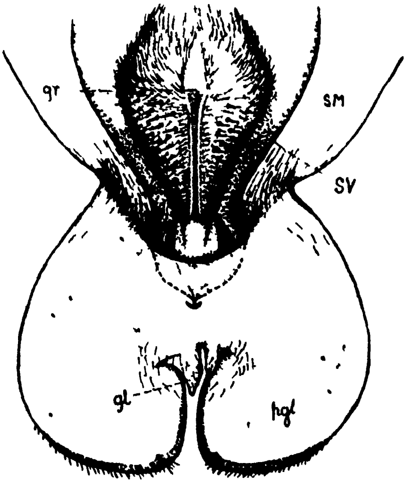


FIG. 13. Inner view of *labium* showing the *salivos* projected within the pocket of the labial membrane. ×15.

gl—Glossa. gr—Groove. pgl—Paraglossa. SM—Submentum. SV—Salivos.

suture between paraglossæ and the premental region gets obscure towards the periphery. The *palpiger* (PGR) which carries a three-segmented *labial palp* (LP), is situated in the corner of the base of the prementum. The last segment of the palp is the longest, and its hemispherical tip is covered with minute sensory setæ.

The inner surface of the labium has a membranous lining which in its proximal region is sharply inflected to form a pocket over the postero-ventral region of the hypopharynx, described further on (Fig. 13. SV). At the point of junction of the hypopharynx to the labial sheath is situated the opening of the salivary duct (Fig. 17. SLO).

Discussion:—Although it has been generally accepted on morphological and embryological evidence that the *labium* of Insects is formed by the fusion of the second maxillæ, the question regarding the *homology* of the various labial structures and especially of the proximal labial sclerites, is still in a doubtful state. Folsom (1922) quoted by Crampton (1928) believes that the mentum and the submentum correspond to the fused stipites and cardines of the second maxillæ respectively. Snodgrass (1928) homologizes the mentum of *Dissostera carolina* with the fused stipites. The lateral articulations of the basal angles of the submentum to the cranium in the same locust, as well as in Orthopteroid Insects in general, suggest to the same author that they are true basal articulations corresponding with those of cardines. Crampton (1928), in the light of embryological evidence, states that neither the submentum nor the mentum has anything to do with the basal sclerites of the maxilla-like appendages forming the labium, and that the uniting cardines of these appendages lie somewhere between the so-called sub-mentum and labial stipites. According to the same author the uniting cardines form what he calls the "medilabium"; the uniting stipites with their endites, the lacinia, form the "labiostipites" with their endites, the glossæ ; the palpifers with their endites, the paraglossæ become the "labial palpigers with their endites the paraglossæ"; and the maxillary palp becomes the "labial palp." Further, according to the same author, the mentum, the submentum and the gular region are secondary developments of a single compound "gulamental plate."

Imms (1931) after discussing the views of various authors including Snodgrass and Crampton, states: "It is probable that in the complete labium the demarkation between the prementum and mentum does not represent originally separate parts and that the two regions as a whole represent a pair of fused stipites. The arrangement of the labial muscles supports this contention." The same author also appears to support the views of Snodgrass in regard to the homology of the submentum with the fused cardines, although he qualifies them (views) as being 'problematical.'

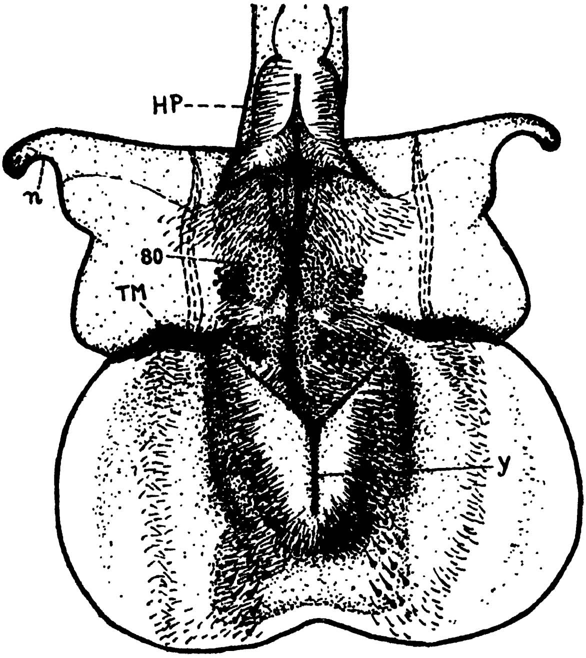


FIG. 14. Inner view of Clypeo-lobrum (*epipharynx*). ×15.

HP—Hypopharynx. n—notch. SO—Sense organs. TM—Torma. Y—Y-shaped suture.

These varied opinions of different authors only indicate that the question of the homology of labial structures is still in an unsolved state, and that it needs to be properly studied from the embryological point of view.

ORAL CAVITY:—The *oral cavity* of this locust occupies a large space and carries on its floor a thick tongue-like lobe called the *hypopharynx* which is "suspended from the ventral wall of the head between the mouth and the base of the labium" (Snodgrass, 1928). The anterior wall of the oral cavity is formed by the inner membranous region of the clypeo-labrum (Fig. 14). Laterally are situated the mandibles and the maxillæ, and the

posterior wall is formed by the inner membranous lining of the labium (Fig. 13).

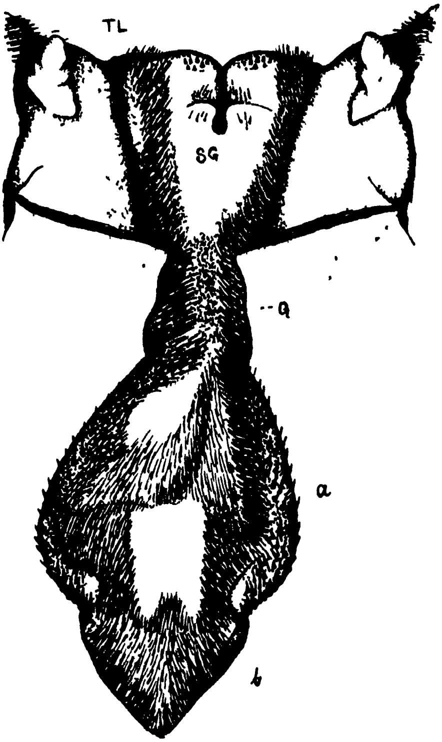


FIG. 15. Anterior view of *hypopharynx*. ×20.

SG—Subgusta. TL—Tritocerebral lobe.

EPIPHARYNX:—The *Epipharynx* (Fig. 14) is not a separate lobe, but is represented by the *inner* membranous wall of the *clypeo-labrum*, and shows some very interesting structures on its surface. The *tormae* (TM) mark apparently the limits of the labral and the clypeal portions of the epipharynx. The surface of the epipharnyx shows asymmetrically developed elevations and depressions which correspond with the uneven surfaces of the right and left mandibles. In the proximal labral area of the epipharynx, one notices a Y-shaped median suture (Y), and the surrounding portion laterally and distally, is occupied by thick rows of spiny hairs directed towards the pharyngeal cavity. The clypeal region of the epipharynx shows three longitudinal grooves, one median and two lateral, all leading towards the pharynx. On each side of these grooves are two groups of sensory organs (SO) in the form of pits and setæ. The proximal region of the epipharynx is all covered with fine hairs directed towards the pharyngeal opening.

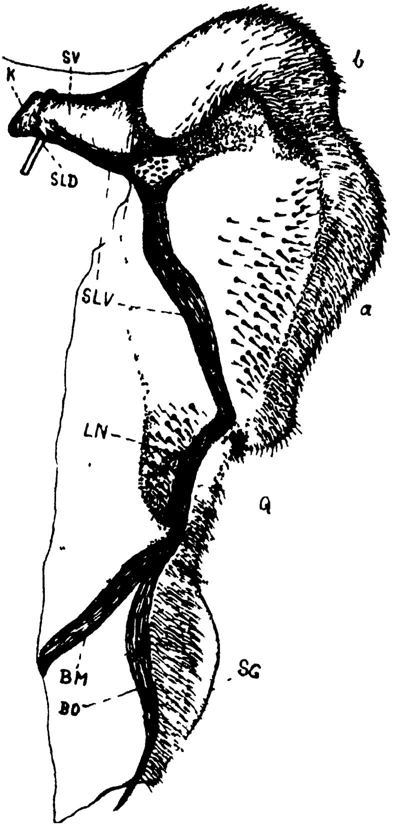


FIG. 16. Lateral view of *hypopharynx*. ×24.

BM—Mandibular bar. BO—Oral bar. K—Keel. LN—Lingula. SG—Subgusta. SLD—Salivary duct. SLV—Salivæ bar SV—Salivos.

HYPOPHARYNX:—The *hypopharynx* (Figs. 15, 16) which forms the floor of the oral cavity, is connected laterally with the inner sides of mandibles and maxillae by membranous extensions. It is an elongate structure divisible into several parts. The bell-shaped proximal region is known as the *subgusta* (SG) (Yuasa, 1920). Behind it comes a small, narrow, neck-like portion (Q), and posterior to the latter is situated a large cordate region (a...b) which according to Yuasa (1920), is the *hypopharynx* proper.

The *subgusta* (SG) has a median furrow leading into the pharyngeal cavity. On either side of this furrow are seen a few sensory setæ. The sides of the subgusta are supported by two pairs of chitinous *bars*. One pair (BO) (*paralinguae*, Yuasa, 1920) runs along its lateral margins towards the pharynx. The other pair (BM) (*linguacuta*) which is less chitinised, runs diagonally across the lateral wall towards the inner angle of the mandibular base. The sides of the subgusta are thickly covered with rows of long hairs.

The narrow neck-like region (Q), situated in front of the subgusta, is also thickly covered with hairs. It is supported on each side by a chitinous bar known as the *lingula* (LN) (Yuasa, 1920). In front of this lies the *hypopharynx proper* (a, b) which is irregularly covered with hairs, and has an uneven surface that corresponds with that of the overlapping mandibles. The distal sub-cordate portion (b) which is demarked from the proximal one (a) by a lateral constriction of its walls, is deflected posteriorly, and forms a terminal process called *salivos* (SV) (Yuasa, 1920). The latter projects within the membranous pocket of the inner lining of the labium (Fig. 13), and carries a groove along its median line, on either side of which prop up rows of hairs and setæ. The region labelled (a) is supported along its sides by a pair of obliquely running chitinous *bars* (SLV) (*salivae*, Yuasa, 1920) which extend posteriorly and support the sides of the salivos (SV).

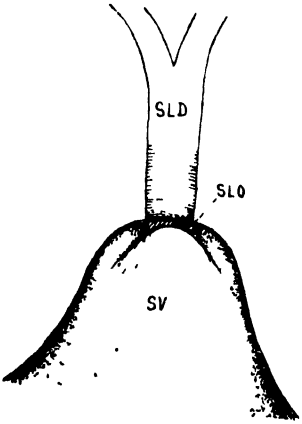


FIG. 17. Tip of *salivos* showing *salivary* duct opening. ×44.

SLD—Salivary duct. SLO—Opening of S. duct. SV—Salivos.

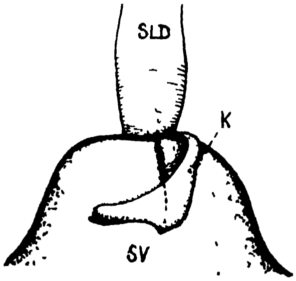


FIG. 18. Tip of *salivos* showing *keel*-structure. ×50.

K—Keel. SLD—Salivary duct. SV—Salivos.

The inner membranous lining of the labium (*vide supra*) is sharply inflected in its proximal region within the labial cavity and thus forms a median sheathlike covering over the hypopharyngeal process, *salivos* (SV) to which it gets attached round the terminal margin. At the junction of the labial sheath to the salivos (SV) opens the salivary duct by a transverse slit (Fig. 17. SLO). Just over this junction the labial sheath develops a keel-like chitinous structure (Fig. 18. K) which, by reason of its peculiar location on the exit passage, presumably regulates the flow of salivary secretion into the mouth cavity.

On either side of the floor of the mouth, between the subgusta (SG) and the inner side of the mandibles (Fig. 15), are seen a pair of thinly chitinised, finger-like lobes (TL) which, according to Snodgrass (1928), are homologous with the "tritocerebral appendages" of the primitive Insect head.

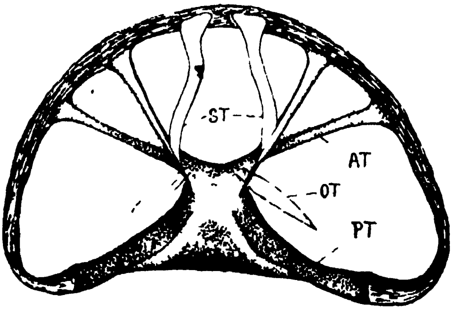


FIG. 19. *Tentorium.* × 8.

AT—Anterior tentorial arm. OT—Oesotendon. PT—Posterior tentorial arm. ST—Supratentoria.

TENTORIUM

The *tentorium* (Fig. 19) which constitutes the endoskeleton of the head is a well-developed chitinous structure, situated within the head-capsule dorsal to the base of the mouth appendages. It has a median elongate 'body' which is concave on the ventral side. From the antero-lateral angles of this body are given off the *anterior tentorial arms* (AT) (*pretentoria*, Yuasa, 1920) which are narrow and twisted at their base, but broaden out distally to meet the lateral corners of the fronto-clypeal ridge. The external *pits* on the fronto-clypeal suture (Fig. 1. pt.) indicate the points of their attachment to the wall of the head-capsule. From the dorsal side of the anterior tentorial arms are given off a pair of thin tentorial processes (ST) (*supratentoria*, Yuasa, 1920) which run dorsally forward, and end blindly in the vicinity of the sub-antennal ridge. From the ventral side of the anterior tentorial arms arises a pair of small tentorial apodemes (OT) (*oesotendons*, Yuasa) which run in a ventral direction. The *posterior tentorial arms* (PT) (*metatentoria*, Yuasa) arise from the posterior angles of the median tentorial body, extend laterally and meet the ventrolateral margins of the post-occipital ridge. The *pits* (Fig. 2. pt) in the mesio-ventral corners of the postgena indicate the points of attachment of the posterior arms to the ventral post-occipital ridge.

CERVICAL REGION

The *neck* (Fig. 20. CV), also called cervicum or eucervix (Crampton, 1917), consists of a narrow membranous area connecting the head with the thorax, ~~and~~ measuring about 3 mm. in breadth (♀). Generally it is not visible from outside, being more or less concealed under the overlapping anterior rim of the pronotum. The neck-membrane is attached to the head-capsule along the post-occipital rim bordering the foramen magnum. With the thoracic region it is connected along the underfolded rim of the pronotum, the mark of attachment being indicated

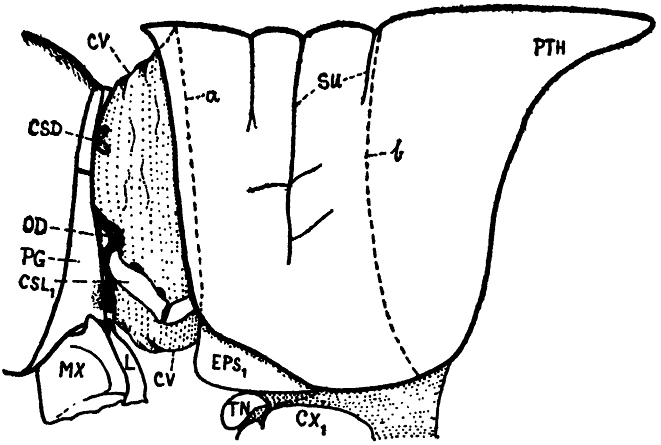


FIG. 20. Lateral view of the *neck* and *prothorax*. ×6.

a—Impressed line along which the neck-membrane is attached to protergum. b—Impressed line along which the interthoracic membrane (MB$_2$) is attached to protergum. CSD—Dorsal cervical sclerite. CSL—Lateral cervical sclerite. CV—Cervical membrane. CX—Coxa. EPS—Episternum. L—Labium. MX—Maxilla. OD—Odontoidea. PG—Postgena. PTH—Metazona. SU—Sulcus. TN—Trochantin.

externally by the presence of a submarginally impressed line (Figs. 20, 25. a). Ventrally the membrane is almost continuous with the anterior margin of the prosternal region (Fig. 21. A...B).

The cervical membrane is strengthened by a number of *sclerites* which, in accordance with their location, are often mentioned as dorsal, lateral, and ventral cervicals. Of these the *lateral cervicals* are more strongly developed and are mainly concerned in the cephalic and prothoracic articulations. They are situated in the side-walls of the cervical membrane and consist, on each side, of two elongate pieces (Fig. 21. CSL$_1$, CSL$_2$) hinged to one another end to end. The anterior sclerite (CSL$_1$) is inserted in a shallow depression at the base of the occipital condyle (OD) of the head-capsule. The posterior sclerite (CSL$_2$) is also inserted in a like concavity situated in the anterior margin of the prothoracic episternum (Fig. 21. PA).

The ventral cervical region (Figs. 21,22. A-B) is distinguished into an anterior membranous area (A) and a posterior chitinous portion (B). The latter is connected with the prosternal region by means of a suture with a strong internal ridge, and carries on its surface three, thinly chitinised, transparent spots indicating the points of muscle-attachment on the inner side.

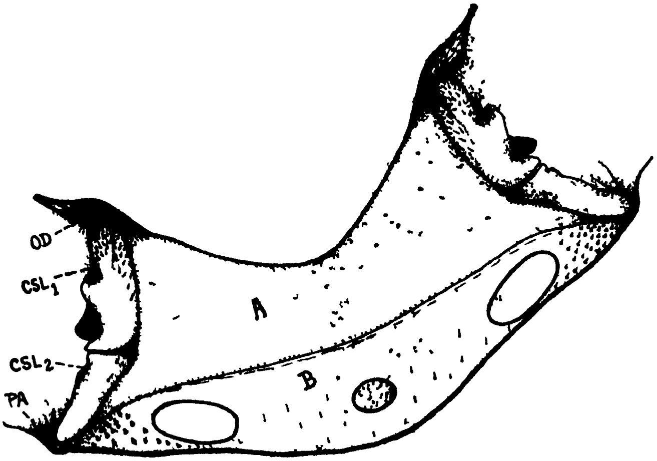


FIG. 21. Ventral view of the *neck* region showing the ventral and lateral cervical sclerites. ×12.

A—Anterior portion of the ventral neck region. B—Posterior portion of the ventral neck region. CSL—Lateral cervical sclerite. OD—Odontoidea. PA—Prothoracic articulatory point with lateral cervical sclerite.

There are no definitely formed dorsal cervicals in *S. gregaria*, but instead, a pair of small infolded chitinised pockets (Fig. 20. CSD) are seen in the dorsolateral corners of the neck-membrane. Each pocket is provided with an internal muscle-tendon arising from its blind end.

The question regarding the *homology* of the cervical region remains still unsolved. The problem seems to hinge upon the morphological nature of the post-occipital rim (including the post-occipital sclerite). "If the latter is an anterior remnant of the labial segment, the neck sclerites may belong to the labial segment, or also to the prothorax; if however, the post-occipital ridge of the head, upon which the anterior ends of the dorsal prothoracic muscles are attached, is the infolding between the head and the prothorax, then the neck can only be a part of the prothorax. The second assumption looks improbable in view of the position of the labial articulations in generalised insects." (Snodgrass, 1928, p 41).

The above remarks amply bear out the hypothetical nature of the homology of the neck-region, and also indicate the importance and necessity of ontogenetic studies for establishing structural homologies in the adult stage of an insect.

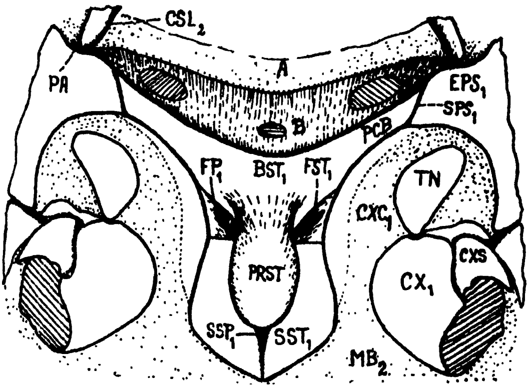


FIG. 22. *Prosternal region.* ×8.

BST—Basisternite. CX—Coxa. CXC—Coxal corium. CXS—Coxal spine. EPS—Episternum. FST—Furcasternite. MB—Intersegmental membrane. PCB—Precoxal bridge. PRST—Prosternal spine. SPS—Sternopleural suture. SSP—Spina-sternal pit. SST—Spina-sternite. TN—Trochantin.

THORAX

The thorax of *S. gregaria*, like that of other jumping Orthoptera, is distinguishable into a distinct prothoracic portion and a "box-like pterothoracic region" formed by the combined meso and meta-thorax. The prothorax is connected with the pterothoracic region by an ample intersegmental membrane (Fig. 25. MB_2) developed on all sides. The intersegmental membrane between the mesothorax and the metathorax disappears completely in the sternal and pleural regions, and is present only on the dorsal side in the form of a narrow intervening strip (Fig. 25. MB_3). The thoracic tergites on the dorsal side usually overlap the succeeding ones in their relation to one another; while the prosternal region on the ventral side is partly concealed under the combined pterothoracic sternal plate (Fig. 24) which projects over it in front.

PROTHORAX :—*Pronotum* :—The *pronotum* (Figs. 20, 23.), also known as *protergum*, is a large saddle-shaped sclerite measuring about 11·5 mm. (♀) along its mid-dorsal length. It extends latero-ventrally and occupies most of the pleural region of the segment. Topographically, it is distinctly constricted in front of its middle and shows three transverse *sulci* (SU) which extend laterally on either side. The sulci divide the pronotum into three small anterior portions and a large posterior one. The anterior divisions known collectively as *prozona* are sub-equal in size and nearly

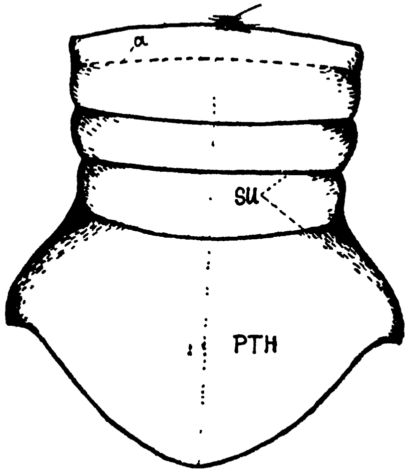


FIG. 23. *Pronotum.* ×6.

Lettering as in Fig 20.

smooth in surface. The large posterior portion known as *metazona* (PTH) has a broadly ovate hind extension which overlaps the mesonotum (Fig. 25). The metazona is broader than long and has an irregularly punctured surface. Along the mid-dorsal line of the pronotum runs a faintly marked ridge-like carina. In profile the pronotum is almost straight with only a slight depression in the middle.

The anterior and posterior margins of the pronotal plate get folded below on themselves before they are joined to the neck-membrane in front (Fig. 25. CV) and to the meso-thoracic intersegmental membrane behind (Fig. 25. MB$_2$). These underfolded portions form a double layer of chitin, closely apposed and strengthened by short internal struts.

Propleuron :—The *pleural region* of a thoracic segment is primarily formed of a single plate divided into two by a secondary vertical infolding of the pleural wall. The anterior portion is known as the *episternum* and the posterior, the *epimeron*. The suture between them is called the *pleural suture* and the corresponding internal ridge is known as the *pleural ridge* (Crampton, 1908; Snodgrass, 1909; Martin, 1916).

The *propleural region* of *S. gregaria* is mostly crowded out on account of the extraordinary development of the pronotal plate.

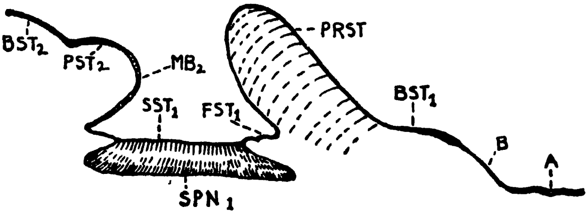


FIG. 24. Mid-ventral *section* through *prosternal* region. ×12.

PST—Presternite (of mesosternum). SPN—Spinasternal process. Other lettering as in Fig. 22.

Only a small piece is visible externally, projecting from beneath the cephalo-ventral margin of the pronotal plate (Fig. 20. EPS$_1$). By turning aside the latter, one, however, finds a triangular sclerite, the *episternum* (Fig. 26. EPS$_1$) behind which is seen another small sclerite, the *epimeron* (EPM$_1$). Between these two sclerites is situated the *pleural suture* (PS$_1$) which internally gives rise to the *pleural ridge*. The ventral margins of the episternum and the epimeron form the border of the prothoracic coxal corium (CXC$_1$).

The episternum is connected with the prosternal region by means of a distinct oblique suture (Fig. 22. SPS_1) located in front of the coxa. Anteriorly the episternum, as mentioned above, gives attachment to the lateral cervical sclerite by means of an excavation in its anterior margin (PA). Internally the ventral end of the pleural ridge projects into the coxal corium and gets articulated to the basal process of the coxa (Fig 27. PCA_1). Just above this coxal process, the pleural ridge gives off a strongly chitinised *pleural apophysis* (PAP_1) which projects across the coxal cavity and becomes strongly united with the corresponding *furcal apophysis* of the furcasternite (Fig. 27. FAP_1) described further on.

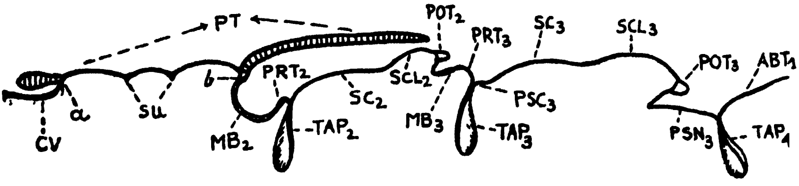


FIG. 25. Mid-vertical *section* through the thoracic *notal* region. ×6.

a—Point of attachment of cervical membrane to protergum. ABT_1—First abdominal tergite. b—Point of attachment of intersegmental membrane between prothorax and mesothorax (MB_2) to protergum. CV—Cervical membrane. MB—Intersegmental membrane. POT—Posttergite. PRT—Pretergite. PSC—Prescutum. PSN—Postnotum. PT—Protergum. SC—Scutum. SCL—Scutellum. SU—Sulcus. TAP—Phragmata. Region between MB_2 and MB_3 = Mesonotum. Region between MB_3 and PSN_3 = Metanotum.

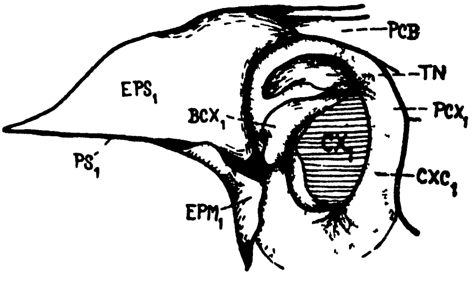


FIG. 26. Prothoracic *pleural* region and *coxal* base. ×8.

BCX—Basicoxite. CX—Coxa. CXC—Coxal corium. EPM—Epimeron. EPS—Episternum. PCB—Precóxal bridge. PCX—Pericoxite. PS—Pleural suture. TN—Trochantin.

STERNUM :—According to Martin (1916) the sternal region of a thoracic segment is composed of five typical sclerites which, commencing from the front, are as follows :—

(1) Presternite (Presternum, Crampton, 1914).
(2) Verasternite (Basisternum, Crampton, 1914)
(Eusternum, Snodgrass, 1910).
(3) Furcasternite (Furcasternum, Crampton, 1914).
(4) Post-Furcasternite (Martin, 1916).
(5) Spinasternite (Spinasternum, Crampton, 1914).

Prosternum :—The prosternal region of *S. gregaria* (Fig. 22) is made of three typical sclerites which are as follows :— (1) basisternite (verasternite), (2) furcasternite, and (3) spinasternite. The *basisternite* (BST_1) carries a blunt finger-like process, the *prosternal spine* (PRST), arising from its mid-posterior region, and pointing obliquely backwards. The spine is about 2·4 mm. in length(♀) and is covered with long flexible hairs. Laterally the basisternite borders on the *coxal corium* (CXC_1), and antero-laterally it sends off a narrow arm, the *precoxal bridge* (Fig. 26. PCB) (Crampton, 1914), joined to the pro-episternum by means of an oblique suture. The anterior border of the basisternite is widely emarginate in front of which is situated the chitinised ventral cervical area (B), connected with it by a suture with a strong internal ridge. Crampton (1918) names this ventral cervical area (B) as "prepectus" after Snodgrass (1910). The latter author, however, in his later publication (1929) homologises it with the *presternite* of Martin (1916).

The *furcasternite* (FST_1) is situated behind the basisternal spine, in the form of a narrow strip with wide lateral plates adjoining the coxal corium (CXC_1). Each lateral plate carries a narrow elongate slit, the *furcal pit* (FP_1), which gives off internally the *furcal apophysis* (Fig. 27. FAP_1). The apophysis of each side projects laterally over the coxal cavity and becomes solidly united with the corresponding *pleural apophysis* (PAP_1) mentioned above.

The furcasternite is connected posteriorly with the sub-cordate *spinasternite* (SST_1) by means of a transverse suture. The spinasternite is marked externally by a median, elongate *pit* (SSP_1) which internally gives rise to a strong unpaired process called the *spine* (Figs. 24, 27. SPN_1). Laterally the spinasternite borders on the coxal corium, and posteriorly it is connected with the intersegmental membrane (MB_2).

Between the pleural wall and the sternal region is situated a membranous area, the *coxal corium* (CXC_1) in which is planted

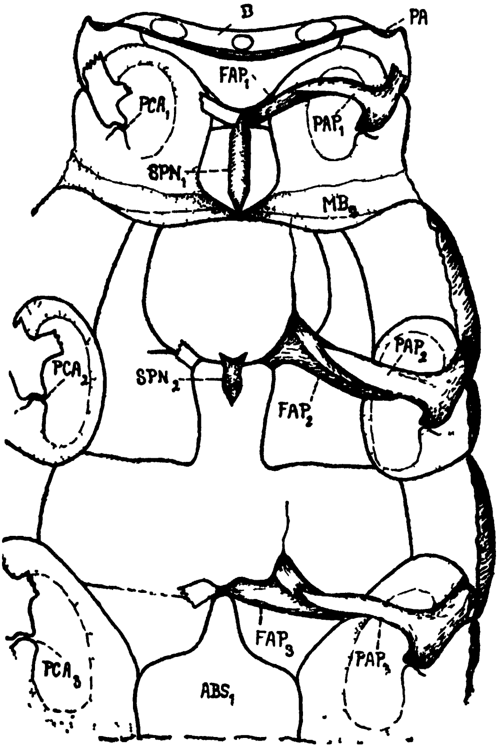


FIG. 27. *Inner view of thoracic sternal region*, showing the spines, apophyses and pleuro-coxal articulations, etc. × 6.

ABS_1—First abdominal sternum. B—Neck region adjoining prosternum. FAP—Furcal apophysis. MB—Intersegmental membrane. PA—Thoracic articulation with lateral cervical sclerite. PAP—Pleural apophysis PCA—Pleurocoxal articulation. SPN—Spinasternal spine.

the coxa (CX_1) of the proleg on each side. The basal structures of the coxa and other segments of the leg are described further on.

MESOTHORAX:-TERGUM :-The dorsal region of a thoracic segment (*tergum* or *notum*) is formed of a single primary plate (*scuto-scutellum*, Crampton, 1908; *eunotum*, Crampton, 1927) which by a secondary modification becomes distinguishable into (1) the *prescutum*, (2) the *scutum*, and (3) the *scutellum*. The intersegmental region between the thoracic tergites is primarily membranous, but in some cases it becomes secondarily chitinised, in part or completely, (the chitinisation being apparently parallel to the development of wings (Martin, 1918)). This secondary chitinisation of the intersegmental membrane gives rise to two sclerotised areas. The anterior sclerotised area, known as the *post-scutellum* or *post-notum* (Snodgrass, 1910), gets firmly attached to the preceding thoracic tergite. The posterior sclerotised area, known as the *pretergite* (Crampton, 1918) or the *precosta* (Snodgrass, 1929), develops a collar-like structure which gets attached to the anterior margin of the succeeding thoracic tergite. The suture connecting the pretergite with the succeeding tergite is known as the *antecostal suture* (*pretergal suture*), with the internal antecostal ridge (Snodgrass, 1929); and the apophyses arising from the internal antecostal ridge are known as the *thoracic phragmata* (Snodgrass, 1929).

Mesonotum :—The mesonotum of *S. gregaria* (Fig. 28) is somewhat rectangular in form and distinguishable into (i) a large anterior subhexagonal scutal region (SC_2) with a pair of antero-lateral prescutal areas (PSC_2), (ii) a median subcordate scutellum (SCL_2) with a pair of lateral oblong parascutellar lobes ($PSCL_2$) and (iii) a posterior, narrow, marginal strip with a deflected rim, the post-tergite (POT_2). The mesonotum is connected with the pronotum by means of an intersegmental membrane (MB_2) the posterior portion of which is converted into a chitinised collar-like area, the pretergite (PRT_2) that joins with the mesoscutal margin by means of the pretergal or antecostal suture. On either side of the pretergite is seen a pair of deep pits (TP_2), situated along the pretergal suture, which internally give rise to the mesothoracic phragmata (Fig. 25. TAP_2).

The *prescutal region* (PSC_2) of the mesonotum is confined to a pair of lateral plates distinctly marked off in the antero-lateral corners of the scutum (SC_2). The shoulder-like antero-lateral corners of the prescutal plates are produced each into a blunt process, the *prealar arm* (PAA_2), against the outer margin of which works the dorsal process of the first basalar epipleurite (IBA_2). The posterior portion of the prescutal plate is deeply chitinised, and its irregularly cleft margin sends off a lateral process, the *suralar process* (SAA_2). The latter carries an excavation (S) in its margin against which moves the basal condyle-like head of the costo-subcostal vein (Fig. 42. CSC).

The *scutum* (SC_2), as mentioned above, is subhexagonal in form. Anteriorly it is margined by the pretergal suture; antero-laterally by the lateral prescutal plates; laterally by the wing base; posterolaterally by the parascutellar lobes ($PSCL_2$); and postero-medially by the scutellum (SCL_2). Along the mid-dorsal line of the scutal region runs a short furrow dividing the scutum into two slightly elevated portions. Just behind the anterior

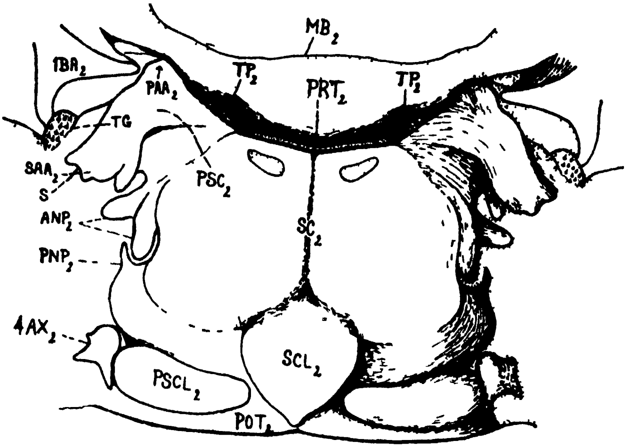


FIG. 28. *Mesonotum.* ×8.

IBA—First basalar sclerite of mesothorax. 4AX—Fourth axillary sclerite of mesothorax. ANP—Anterior notal wing process. PAA—Prealar process. PNP—Posterior notal wing process. PSCL—Parascutellar lobe. S—Socket-like depression in the margin. SAA—Subalar process. TG—Tegula. TP—Pits of thoracic phragmata. Other lettering as in Fig. 25.

margin of the scutum, on either side of this median furrow, are seen two small subpyriform, unchitinised areas which indicate the site of muscle-attachment internally.

The lateral margin of the scutum, on either side, is deeply chitinised, and its irregular outline develops into a furcate *anterior notal wing-process* (ANP_2) and an unforked posterior one (PNP_2). Against the furcal angle of the anterior notal wing-process works the neck of the first axillary sclerite (Fig. 42. AX_1) of the meso-thoracic wing-base. The inner margin of the same sclerite is hinged to the lateral border of the posterior notal wing-process (Fig. 42. PNP).

The *scutellum* (SCL_2) is situated in the mid-posterior region of the mesonotum and is subcordate in form. All along its lateral and posterior margin runs a suture with a strong internal ridge. The external surface of the scutellum is convex and is covered with long flexible hairs.

On each side of the scutellum is seen an oblong convex lobe ($PSCL_2$) thickly covered with long flexible hairs. It is bounded on all sides by a suture giving rise to a strong internal ridge. Crampton (1918) named these lobe-like areas on either side of the scutellum as *parascutellar* lobes. Snodgrass (1929) mentions them as posterolateral lobes of the scutum.

Posterior to the scutellum and the parascutellar lobes lies a narrow marginal tergal strip, the *post-tergite* (POT_2) (Crampton 1918), which has its border folded below on itself. It is connected with the metanotum by means of the intersegmental membrane (Fig. 25. MB_3). The latter being unchitinised, no post-scutellum (postnotum) is developed in the case of mesonotum.

Mesosternum :—The intersegmental membrane between the meso-and meta-thorax disappears completely in the pleural and sternal regions, with the result that the sternal plates and the pleural walls of these segments are firmly united to each other to form a strong chitinous structure.

The mesosternal region (Fig. 29) projects in front over the posterior portion of the prosternum. It consists of a broad,

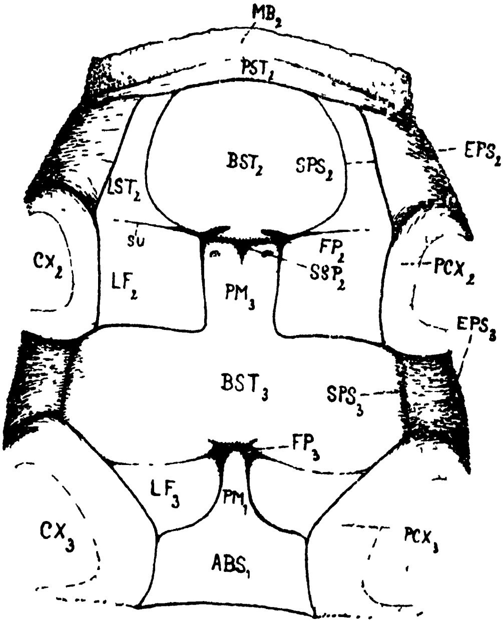


FIG. 29. Ventral view of the *meso-and meta-sternal* regions. × 6.

ABS—First abdominal sternite. BST—Basisternite. CX—Coxa. EPS—Episternum. FP—Furcasternal pit. LF—Furcasternal lobe. LST—Latero-sternite. MB—Intersegmental membrane. PCX—Pericoxite. PM—Median process. PST—Presternite. SPS—Sternopleural suture. SSP—Spinasternal pit. SU—Suture.

median, subcordate plate, in addition to a pair of narrow ones situated laterally. The broad median plate is homologous with the *basisternite* (BST$_2$) and is joined, in front, to a narrow chitinised *presternal* strip (PST$_2$) which is continous with the inflected intersegmental membrane (MB$_2$) between the pro-and meso-sternal regions. The *furca* and *spina-sternites* which are so well developed in the prosternal region, are reduced in the mesosternum, being represented only by a pair of lateral *furcal pits* (FP$_2$), and an unpaired median *spinal pit* (SSP$_2$) respectively. The pits in question are situated along the line of junction of the basisternite with the meta-sternal region. On each side of the basisternite is situated a narrow, elongate, lateral plate which posteriorly develops into a quadrate lobe. A short suture (SU) extends laterally from the furcal pits across this lateral plate dividing it incompletely into a narrow anterior and a quadrate posterior sclerite. The narrow anterior sclerite on each side may represent the *latero-sternite* of Crampton (1914) (Fig. 29. LST$_2$), while the quadrate posterior sclerite is named as the *mesosternal lobe* by systematists (Crampton, 1918). Morphologically, however, Snodgrass (1929) interprets the latter as the "lateral lobes of meso-furcasternite". Between these furcasternal lobes (LF$_2$) is "dove-tailed" the median rectangular prolongation (PM$_3$) of the metasternal basisternite (BST$_3$). The laterosternite is joined laterally to the ventral arm of the mesoepisternum (EPS$_2$) by means of a faintly marked suture (SPS$_2$).

Internally (Fig. 27) the posterior margin of the basisternite gives rise to a strong ridge bearing a median snout-like *spine* (SPN$_2$) and a pair of lateral *furcal apophyses* (FAP$_2$). Each apophysis has a strong basal stalk with a flattened lateral extension against which is apposed a similarly constructed *pleural apophpsis* (PAP$_2$) of each side.

Mesopleuron:—The mesopleuron (Fig 30) consists of an anterior *episternal* (EPS$_2$) and a posterior *epimeral* plate (EPM$_2$), and between them runs the sub-vertical *pleural suture* (PS$_2$). Anteriorly the episternum is connected with the intersegmental membrane (MB$_2$) situated between the pro- and meso-thorax, and also with the lateral arm of the ventral presternal sclerite (PST$_2$). The ventral margin of the mesopleural region forms mostly the border of the *coxal corium* (CXC$_2$) and meets, in front, the laterosternite of the mesosternum (Fig. 29. LST$_2$) by means of a suture (SPS$_2$), as mentioned above. Dorsally the pleural margin is slightly irregular in outline and sends up a strongly chitinised median process (PWP$_2$) which serves as a pivot to the base of the mesothoracic tegmen on each side.

The pleural suture has a strong internal ridge which terminates ventrally in a socket-bearing process with which articulates the basal process of the coxa (Fig. 27. POA_2). Slightly dorsal to this *pleuro-coxal articulation* is given off internally an apophysis (PAP_2) which projects across the coxal cavity and rests against the corresponding *furcal apophysis* (FAP_2) of the mesosternum (as mentioned above).

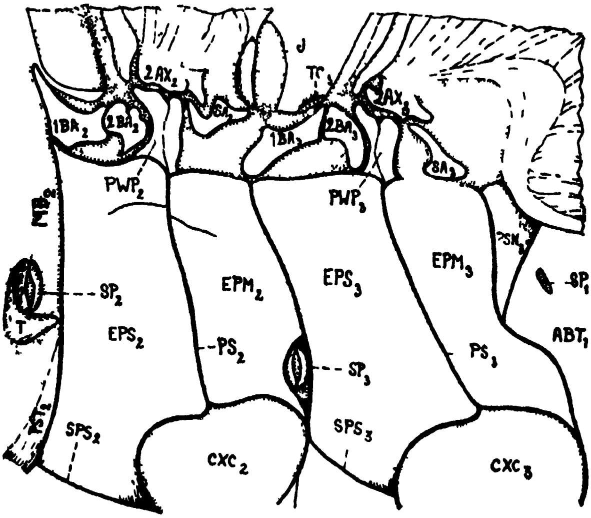


FIG. 30. *Pleural* region of the *meso-and meta-thorax.* ×6.

IBA—First basalar sclerite. 2BA—Second basalar sclerite. 2AX—Second axillary sclerite. ABT—First abdominal tergite. CXC—Coxal corium. EPM—Epimeron. EPS—Episternum. J—Jugal area of wing. MB—Intersegmental membrane. PS—Pleural suture. PSN—Postnotum, PST—Presternite. PWP—Pleural wing process. SA—Subalar sclerite. SP—Spiracle. SPS—Sterno-pleural suture. T—Peritremal process. TG—Tegula.

Between the pleural margin and the wing-base, are situated a certain number of sclerites which support the wing-base from below. These along with the basal region of the wing are described in detail further on.

METATHORAX:—*Metanotum:*—The metanotum of *S. gregaria* (Fig. 31) which is about 6 mm. in length (♀) including the postnotal plate, is longer than the mesonotum which is only 4·8 mm. in length (♀). It is distinguishable into (i) a narrow anterior prescutal region (PSC_3), (ii) a large scutal area (SC_3) with a pair of parascutal lobes ($PSCL_3$), (iii) a subcordate scutellum

(SCL_3), (iv) a narrow post-tergal strip with deflected rim (POT_3) and (v) a strongly developed postnotal plate (PSN_3).

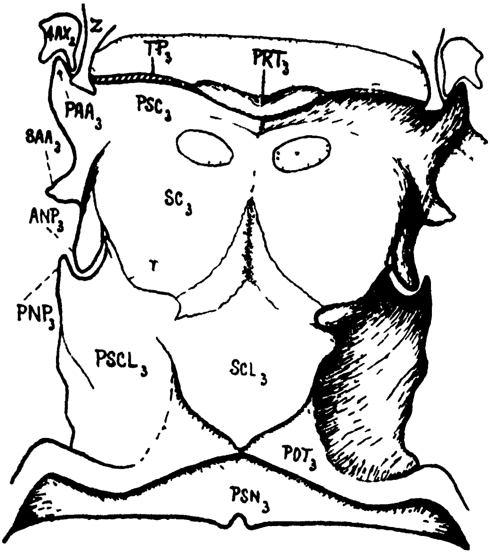


FIG. 31. *Metanotum.* ×8.

4AX—Fourth axillary of mesothorax. PSN—Postnotum. r—Ridge. Z—Posterior process of the parascutellar ridge of the mesothorax. Other lettering as in Fig. 28.

The narrow intersegmental membrane (Fig 25. MB_3) which connects the metanotum with the mesonotum is completely hidden from view by the overlapping posterior margin of the latter. The posterior portion of the membrane forms a median deeply chitinised collar-like piece, the *pretergite* (PRT_3), connected with the metanotum by means of the pretergal or antecostal suture. On either side of the pretergite are deep *pits* (TP_3) located in the pretergal suture, which internally give rise to the strongly developed *metathoracic phragmata* (Fig. 25. TAP_3).

The *prescutal* region (Fig. 31. PSC_3) of the metanotum is limited to a narrow anterior strip widening out laterally to form a shoulder-like area on either side. The antero-lateral corner of each prescutal area sends forward a conical process (PAA_3), the *prealar process*, which articulates with the fourth *axillary* sclerite ($4AX_2$) of the mesothoracic wing-base. The internal ridge of the parascutellar suture of the mesonotum (*vide supra*) sends a postero-lateral arm (Z) which works freely against the base of the meta-prescutal *prealar* process (PAA_3), mentioned above. Posteriorly the prescutal region sends off a lateral extension known as the *suralar* process (SAA_3).

Behind the prescutal area is situated the broad *scutal* region (SC$_3$). It shows a mid-dorsal furrow which becomes deeper and wider posteriorly, with the result that the right and left halves of the scutum appear as two distinct, slightly elevated areas. Anteriorly on either side of this furrow are seen a pair of subpyriform, unchitinised spots known as muscle-impressions. In its mid-posterior region is seen another wedge-shaped, weakly chitinised spot with wavy margins which also marks the site of internal muscle attachment. The lateral margin of the scutum develops on each side a strongly chitinised process directed posteriorly. It is known as the *anterior notal wing-process* (ANP$_3$). The scutal region extends behind, on each side of the medially placed scutellum (SCL$_3$), in the form of a postero-lateral scutal area (*parascutal area*), demarked from the principal scutal region by a diagonal *ridge* (r). The antero-lateral corner of this parascutal area shows a deep emargination into which projects the anterior notal wing-process (ANP$_3$), mentioned above. The antero-lateral prolongation of the same area constitutes the *posterior notal wing process* (PNP$_3$) of the metanotum.

The *scutellum* (SCL$_3$), as mentioned above, is situated just behind the wedge-shaped unchitinised muscle-impression of the scutum, between the lateral parascutal areas. It is sub-cordate in form with a broad anterior base and is thickly covered with hairs. Behind the scutellum runs the narrow tergal strip known as the *post-tergite* (POT$_3$) which is also thickly covered with hairs. Laterally the post-tergite sends off a long chitinised arm which supports the base of the anal area of the hind wing on each side. The posterior rim of the post-tergite is sharply bent below on itself, and is joined to the chitinised intersegmental area, the *post-scutellum* (postnotum) of the metanotum (Figs. 25, 31. PSN$_3$).

Metasternum;—The sternal region of the metathorax (Fig. 29) is wider than that of the mesothorax, and consists of a single large plate with a pair of indistinctly separated, posterior lobes. The broad single plate is the *basisternite* (BST$_3$). The furcasternite is attenuated, its only remnant being a pair of *furcal pits* (FP$_3$), situated in the mid-posterior margin of the basisternite. The spinasternite disappears altogether from the metasternal region.

The basisternite sends forward a median, anterior, rectangular proccss (PM$_3$) which is 'dovetailed' between the lateral lobes of the meso-furcasternite (LF$_2$). Laterally the basisternite is joined to the meta-episternal plate by means of a distinct suture (SPS$_3$) across the precoxal bridge. Posteromedially it is connected with the first abdominal sternite (ABS$_1$) by means of a suture with a strong internal ridge. This suture which also carries the *furcal pits* (FP_3) indicative of internal furca-sternal apophyses, extends laterally on each side across the posterolateral areas of the metasternum. The latter have often been referred to as *metasternal lobes* by systematists, but morphologically Snodgrass interprets them as the lateral lobes of the *metafurcasternite* (LF_3). Internally (Fig. 27) the furcal ridge is strongly developed, and so are the *furcal apophyses* (FAP_3), which rest against the corresponding *pleural apophyses* (PAP_3).

Metapleuron :—The metathoracic pleural region (Fig. 30) consists of an anterior *episternal plate* (EPS_3) and a posterior *epimeron* (EPM_3). Anteriorly the episternum is connected with the mesopleural region by means of a distinct suture. Posteriorly the epimeral margin touches the lateral extension of the post-notal plate (PSN_3) and the first abdominal tergite (ABT_1). Ventrally the metapleural margin forms mostly the border of the coxal corium (CXC_3), in front of which it meets the metasternal region to form the *precoxal bridge*, showing the sterno-pleural suture (SPS_3) across the same. Dorsally the metapleuron sends upwards a strongly chitinised process along the pleural suture. It is called the *pleural wing process* (PWP_3) which serves as a pivot-like support to the base of the metathoracic wing on each side. On either side of this process, between the base of the wing and the pleural margin, are situated the alar epipleurites which are described in detail elsewhere.

The *pleural suture* has a strong internal ridge which terminates ventrally in a socket-bearing process that articulates with the basal process of the hind coxa (Fig. 27. PCA_3). Slightly dorsal to this *pleuro-coxal articulation* is given off internally an apophysis (PAP_3) which projects across the coxal cavity and rests against the corresponding furcal apophysis (FAP_3) of the metasternum, as mentioned above.

LEGS

The thoracic segments of *S. gregaria*, like all other insects in general, carry each a pair of well-developed *legs*, situated along the sterno-pleural region on each side. These ventro-lateral appendages of the thorax are essentially meant for the terrestrial type of locomotion, which, in the case of the desert locust, consists mostly of hopping or jumping from place to place, the walking mode being resorted to only occasionally. In adaptation to its jumping habit the hind legs of the locust are the most strongly developed of all, Each *leg* is composed of five typical segments known as coxa (CX), trochanter (TR), femur (FM), tibia (TB), and a three-segmented tarsus (TS) which bears a terminal praetarsal region consisting of a pair of claws (CL) and a median arolium (AR). The *coxa* of each leg is planted in an oval membranous area known as the *coxal corium* (Figs. 26, 32, 33. CXC). The area of the coxal corium is smaller in the case of the front legs (Fig. 26), a little wider in the middle legs (Fig. 32), and largest in the case of the hind ones (Fig. 33). The coxal corium is bordered mesially by the sternal region of each segment, laterally by the ventral margin of the pleural wall, anteriorly by the *precoxal bridge* (PCB) (formed by the junction of the ventral arm of the pleural and lateral arm of the sternal regions on each side), and posteriorly by the intersegmental membrane. The intersegmental membrane between the meso-and metathorax having disappeared, the posterior boundary of the meso-coxal corium (Fig. 32) is bounded directly by the anterior margin of the metasternal and metapleural regions. The coxal corium of each coxa is chitinised along its sternal margin to form the *pericoxite* (PCX). The pericoxite is strongly developed in the case of the metacoxa (Fig. 33. PCX). Between it and the base of the coxa, the coxal corium is deeply inflected. On the pleural side the coxal corium of each leg is interrupted by the ventral continuation of the pleural suture.

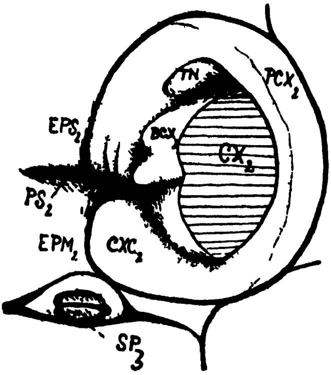


FIG. 32. Base of *middle coxa.* ×8.

SP—Spiracle. Other lettering as in Fig. 26.

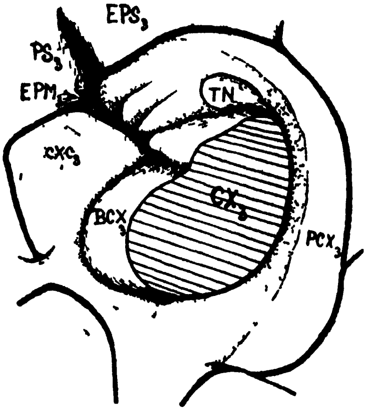


FIG. 33. Base of *hind coxa.* ×8.

Lettering as in Fig. 26.

In the anterior corner of the coxal base is situated a subtriangular sclerite, the *trochantin* (TN). The trochantin is considered to be derived from the ventral margin of the episternum,

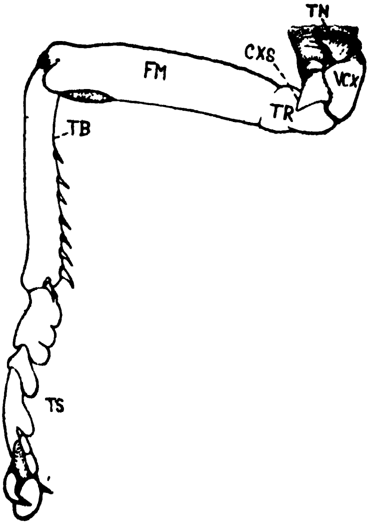


FIG. 34. *Prothoracic leg.* ×4.

CXS—Coxal spine. FM—Femur. TB—Tibia. TN—Trochantin. TR—Trochanter. TS—Tarsus. VCX—Veracoxa.

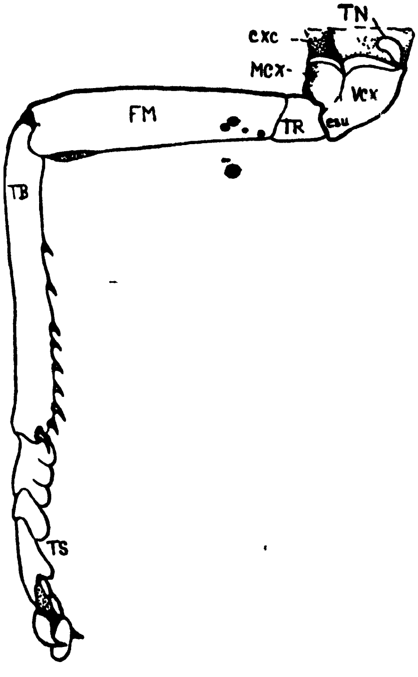


FIG. 35. *Mesothoracic leg.* ×4.

CSU—Coxal suture. CXC—Coxal corium. MCX—Meron of coxa. Other lettering as in Fig. 34.

especially, the precoxal bridge (PCB) (Martin, 1916). In the *S. gregaria*, however, it has lost its episternal or precoxal connection and is found to be articulating with the anterior corner of the coxal base by means of a small condyle-like process. The trochantin is more strongly developed in the front leg than in the case of the other two pairs.

The base of each coxa is somewhat deeply reniform. The point of emargination, which is deeply sunk within the coxal cavity, sends in a blunt process which articulates with the shallow callosity in the broad ventral edge of the pleural ridge. This is the single articulation of the coxa to the body-wall (Fig. 27. PCA).

On the pleural side of the base of the coxa lies a narrow

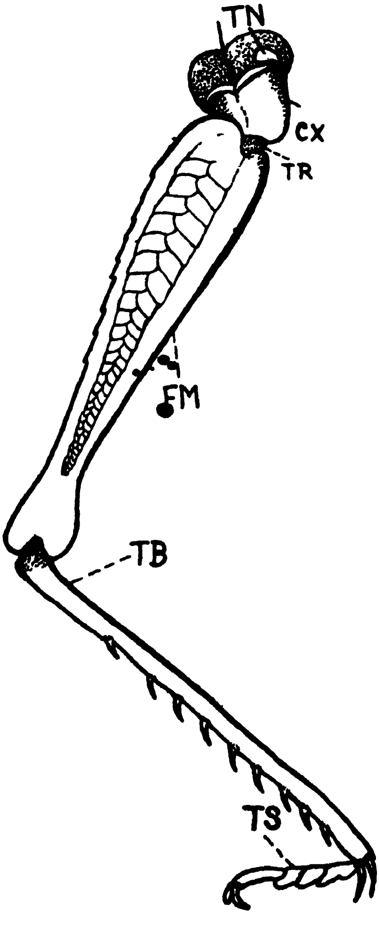


FIG. 36. *Metathoracic leg.* ×1½.
CX—Coxa. Other lettering as in Fig. 34.

elongate sclerite, the *basicoxite* (BCX). It starts anteriorly at the point of articulation of the trochantin to the coxal base, and runs along the emarginated side of the coxal base as far back as its posterior extremity.

Across the basicoxite and the coxa proper runs a suture, the *coxal suture* (Figs. 34, 35, 36. CSU) which proximally is continuous with the pleural suture in the coxal corium. It thus divides the coxa into an anterior portion, the *vera-coxa* (VCX) and a posterior portion, the *meron* (MCX). The coxal-suture, in the case of the front coxa, is found to take a winding course; in the case of the middle and hind coxæ, however, it traces almost a straight path. In the case of the front coxa, the distal end of the veracoxa is produced in the form of a conical process, the *coxal spine* (Fig. 34. CXS), which is absent in the middle and hind coxæ.

Internally the coxal base gives off a number of *apodemous processes* for muscle-attachment. According to the location from which they originate, they may be referred to as trochantinal, anterior basicoxal, mid-basicoxal, and posterior basicoxal apodemes. In the case of the front coxa there are three trochantinal, one anterior basicoxal, two mid-basicoxal, and three posterior basicoxal apodemes. In the case of the middle coxa there are three trochantinal, one anterior basicoxal, two mid-basicoxal and three posterior basicoxal. In the case of the hind coxa there are two trochantinal, one anterior basicoxal, one mid-basicoxal and three posterior basicoxal.

The *second* segment of the leg is the *trochanter* (Figs. 34, 35, 36. TR) which is strongly developed in the case of the first two pairs of legs, but is only a narrow ring-like sclerite in the case of the hind pair. It is connected with the coxa by a movable dicondylic type of articulation which allows it to move in a sub-vertical plane within an angle of 90 degrees. The two articulatory points are situated in the antero-ventral and postero-dorsal corners of the distal coxal margin which forms sockets to receive the trochanteral condyles. Between these articulatory points the dorsal margins of the coxa and of the trochanter are broadly emarginate, and the area between them is occupied by an ample articular membrane (corium) which, by reason of its inflection, facilitates the subvertical movement of the trochanter.

Internally the trochanteral base gives off one mid-dorsal and two mid-ventral *apodemes*. Distally the trochanter is immovably fixed to the base of the femur.

The *femur* (FM) is a slender, elongate, rodlike piece in the front and middle legs; in the case of the hind legs, however, it is a very strongly developed segment, in adaptation to the jumping habit of the locust. The inner and outer surfaces of the hind femur, *in situ*, are broadly flattened in the proximal region and taper gradually towards the distal end. The flattened region bears on either side rows of muscle-impressions in the form of a "fish-bone pattern of a double series of oblique ridges". Along its ventral side is seen a narrow longitudinal groove, the *femoral groove* in which the tibia rests when folded below. In the proximal portion of this groove is found a small tubercle planted in a minute socket, which may possibly have a sensory function.

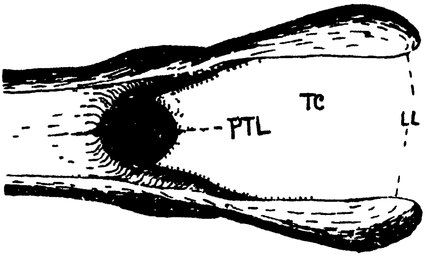


FIG. 37. Ventral view of the distal *femoral end* showing the lobes and the median blackened *patella*.

LL—lateral lobes. PTL—Patella. TC—Tibia corium.

The distal end of the *femur* is somewhat swollen, and has its sides expanded posteriorly in the form of a pair of broad, chitinous, plates (Fig. 37. LL). Between these plates intervenes a deep emargination on the ventral side, at the base of which is situated a small bowl- shaped sclerite known as the *patella* (PTL). The latter is deeply chitinised and is only partly visible from the ventral side, major portion being covered by the articular membrane (TC) of the femoro-tibial joint. The dorsal margin of the femoral extremity is broadly concave and carries laterally a deep socket on each side.

The *femoro-tibial joint* is of a dicondylic type and allows the tibia to work in a vertical plane within a field of 180 degrees. The proximal extremity of the *tibia* is knob-like in appearance and bent nearly at right angles. The knob-like portion carries laterally a pair of condyle-like processes which work in the sockets situated in the dorso-lateral margins of the distal extremity of the femur (*vide supra*). In the articulation of the femoro-tibial joint, the tibial knob, at the time of extreme flexion, bumps against the broadly concave dorsal margin of the distal extremity of the femur, and prevents retroflexion. The femoro-tibial joint is provided with an ample articular membrane known as the *tibia-coria* (Macgillivray, 1923) which is capable of great flection.

The *tibia* (TB), the fourth segment of the leg, has the form of a slender rod and is almost as long as the femur. It is provided with two rows of strongly developed spines, the *tibial spines* with dark tips. In the case of the front and the middle tibiæ, the spinal rows are situated on the ventral side; in the case of the hind tibia they are situated on the dorsal side. In addition to these rows of spines, the hind tibia also carries two pairs of strongly developed, slightly curved, elongate *spurs* at its distal extremity. The spurs are capable of a slight movement and are brought into action when the insect takes a jump. The role played by the hind tibia in saltation is very important, and the muscles instrumental in this movement are attached to a pair of strong internal apophyses which arise from the dorsal and ventral edges of the tibial knob, and extend within the femoral cavity. Similar types of internal apophyses are also found in the case of the front and middle tibiæ, but they are not so strongly developed as those of the hind one.

The number of spines in the rows on the tibia is variable. The number is not constant for particular rows nor in different tibiæ of the same specimen. Typically, however, the spines are arranged as follows:—

		Front leg.	Middle leg.	Hind leg.
♀	Right leg ...	8+7	8+7	11+9+4
	Left ,, ...	8+9	8+9	12+9+4
♂	Right leg. ...	8+7	9+ 9	11+11+4
	Left ,, ...	8+7	9+10	12+ 9+4

The *tarsus* (TS) of each leg is composed of three proximal sub-segments and a terminal claw-bearing portion, the prætarsus (Fig. 38). The tibia-tarsal joint is dicondylic and works on the same plan as the femoro-tibial joint. The first two tarsal sub-segments carry on their ventral surface four cushion-like *pads* (PD) (*euplantulae*, Crampton), the first one carrying three and the second carrying one. In the case of the front and middle legs these tarsal pads are all bilobed; in the case of the hind leg the first one is unpaired, the second may or may not be paired, the third and the fourth are always paired or bilobed. The third tarsal subsegment is slightly convex on its dorsal side and carries a median elongate euplantula on its ventral surface.

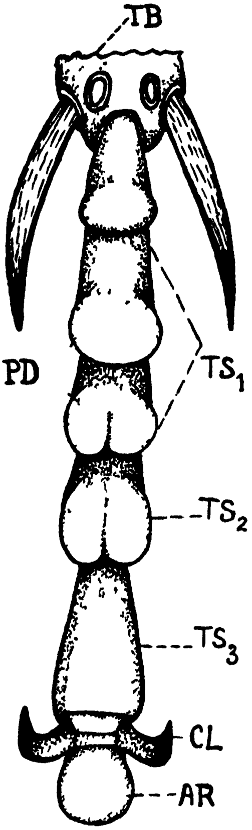


FIG. 38. *Tarsal* region of the leg. ×8.

AR—Arolium. CL—Claw. PD—Tarsal pads. TB—Tibia. TS—Tarsal segment.

The terminal claw-bearing portion, also known as the *praetarsus* (Fig. 39), carries a pair of strongly developed lateral *claws* (CL) and a median oval lobe, the *arolium* (AR). At the base of the arolium on the ventral side are situated two plate-like sclerites known as the *unguitractor plate* (UP) and the *planta* (PN) (Snodgrass, 1929) respectively. The tarsal pads as well as the arolium carry a few sensory setæ on the surface. The following table gives the average length in mm. of the various segments of the legs of *S. gregaria* (♀) between the longest points :—

	Coxa.	Trochanter.	Femur	Tibia.	Tarsus.			
					1	2	3	4
Front leg. ...	2·4	2·2	8	8·1	2·3	1·3	2·4	1·3
Middle leg. ...	2·5	1·6	9	10·8	2·4	1·5	2·5	1·4
Hind leg. ...	4·5	1·3	29	28	4	1·8	3	1·5

Comparing these measurements one finds the trochanter to be strongly developed and longer in the front leg and to some extent in the middle leg. The hind femora and tibiæ are about three times longer than those of the front and middle legs.

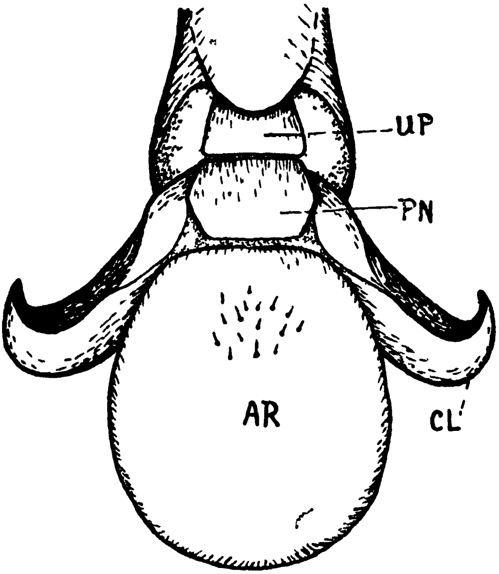


FIG. 39. *Pretarsal* joint enlarged.

AR—Arolium. CL—Claw. PN—Planta. UP—Unguitractor plate.

WINGS

The desert locust, like all other Orthopteroid insects, carries two pairs of *wings*, attached to the body in the tergo-pleural region of the meso- and meta-thorax on each side. Of these thoracic dorsolateral appendages, serving essentially for flying through air (ærial locomotion), the front pair attached to the mesothorax, is rather narrow and thickened, and of a leathery consistency, and is known for that reason, as *tegmina*. The hind pair, attached to the metathorax, is very broad in its expanse, and thin and membranous in its formation, and so constitutes the *wings* proper of this insect. Both pairs attain a great length in the adult stage and usually extend far beyond the tip of the abdomen. The average measurements of the tegmen and the wing are 61 mm. and 59.5 mm. in the female, and 54 mm. and 51 mm. in the male respectively.

In a state of rest, the broadly expansible hind wings get folded and remain concealed under the tegmina, both pairs roofing over the thorax and abdomen dorsolaterally. This folding is made possible by the development of a conspicuous longitudinal fold, the *anal fold*, which divides the tegmen and the wing into an anterior *preanal* and a posterior *anal* region. The anal area of the hind wing is very extensive, and is further split up by the development of a large number of *sub-anal folds* (13 in the desert locust), by means of which the hind wing is capable of folding in a fan-like fashion. When flying, both the tegmina and wings spread out laterally at right angles in the horizontal plane.

VENATION :—The tegmina and the wings possess a skeletal framework in the form of chitinised *veins* which lie embedded in the membranous integument Morphologically, the wing-veins are tracheal in origin, and are the result of subsequent chitinization of the wing-integument along the trachæ and their branches (Comstock, 1918). In their number, branching and distribution, the wing-veins of an adult insect closely follow the tracheation of the wing-pads of its post-embryonic stages. The study of the tracheation of the post-embryonic wing-pads of an insect would thus supply an unmistakable key to the interpretation of the wing veins of the adult.

Referring to the venation of the *desert locust* (Figs. 40, 41.), the principal wing veins found here are costa, sub-costa, radius, median, one or two cubitals and two or more anals. In the preanal region of the tegmina and the wings of this locust are situated the *costa* (C), the *subcosta* (SBC), the *radius* (R) with its *radial sector* (RS) and distal sub-branches, the *median* (M) with its two branches, and one or two *cubitals* (CU) with the cubital sector if any. The costa and the subcosta have a common sclerotised base (Figs. 42, 43). The tegminal costa is submarginal, while the "alar" costa is marginal in its situation. The subcosta, the radius and the median, all run close to each other in both the front and hind pairs. Regarding the cubital veins, the *tegmen* carries a single cubital vein which gives off proximally a *cubital sector* (CUS) and distally a few secondary branches. The *hind wing* carries two unbranched cubital veins of which the *first cubital* (CU_1) is situated between the median and the anal fold, while the *second* (CU_2) runs along the roof of the same fold.

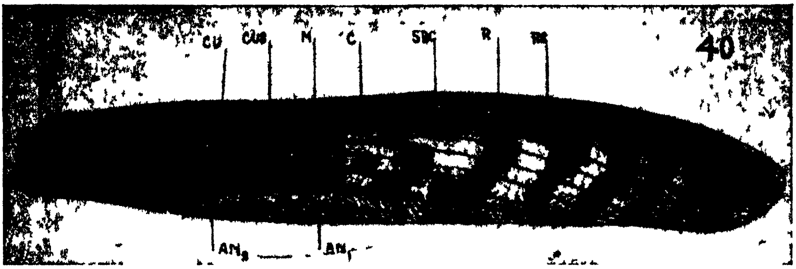


FIG. 40. *Tegmen* (front wing) × Nearly 2.

AN—Anal vein. C—Costa. CU—Cubital. CUS—Cubital sector. M—Median. R—Radius. RS—Radial sector.—SEC. Subcosta

FIG. 41. *Hind Wing.* × Nearly 2.

AN—"convex" anal. an—"concave" anal. Other lettering as in Fig. 40.

The anal region of the *tegmen* is provided with two anal veins of which the *first anal* (AN_1) runs close to the posterior margin of the anal fold, while the *second anal* (AN_2), situated behind, ends blindly without reaching the anal margin. The anal region of the *hind-wing* is capable of folding fan-like, in adaptation to which thirteen secondary folds are developed, which are all supported by *thirteen anal veins* (AN_{1-13}). These veins arise from the basal *anal shaft* and run along the roof of the secondary anal folds, as mentioned above.

WING-SCLERITES:—The tegmina and the wings are attached to the thorax between the notal and pleural regions on each side. The attachment is membranous and is supported by a number of articulatory sclerites situated above and below the wing-base. Those above are called the *axillary sclerites* of which there are four in each wing-base. Those below are known as the *epipleurites* of which there are three in each wing-base. In addition to the presence of these alar sclerites, the bases of the wing veins form strongly sclerotised areas, and the tergo-lateral and the pleuro-dorsal margins (*vide supra*) are also structurally modified in connection with wing-articulation.

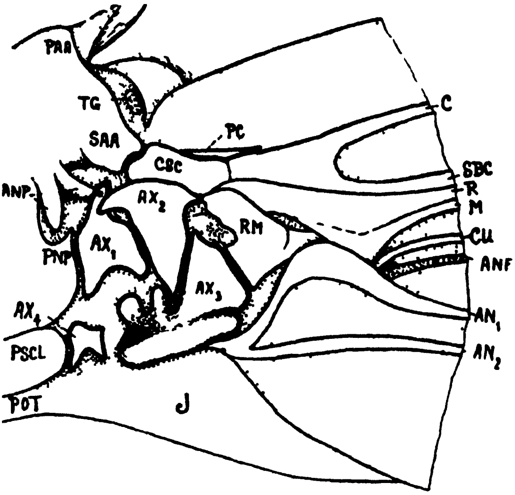


FIG. 42. Dorsal view of the *base of the tegmen* showing the wing sclerites. × 8.

AN—Anal vein ANF—Anal fold. ANP—Anterior notal wing process AX—Axillary sclerite. C—Costa vein. CSC—Costo-sub-costal basal sclerite. CU—Cubitus vein. J—Jugal area. M—Median vein. PAA—Prealar process (Fig. 28). PC—Precostal sclerite. PNP—Posterior notal wing-process. POT—Post-tergite. PSCL—Parascutellar lobe. R—Radius vein. RM—Radio-median sclerite. SAA—Suralar process (Fig 28). SBC—Subcosta vein. TG—Tegula.

Basal region of the tegmina:—The *first axillary sclerite* (Fig. 42. AX_1) occupies a diagonal position along the sides of the anterior and posterior notal wing-processes of the mesoscutum (ANP, PNP). It has a median, anterior, curved, stalk-like process which works against the angle between the arms of the *anterior notal wing process* (ANP), and allows a similar lateral process of the second axillary (AX_2) to rest against its own curved base. The mesial margin of the first axillary sclerite is movably hinged to the side of the *posterior notal wing-process* (PNP).

The *second axillary sclerite* (AX_2), situated lateral to the first, is a deep-rooted sclerite which ventrally abuts on the surface of the wing-base (Fig. 30. $2AX_2$). Anteriorly it is immovably joined to the head of the costo-subcostal basal sclerite (CSC). Posteriorly it terminates in a conical process which is received into a deep notch in the anterior margin of the third axillary (AX_3).

The *third axillary sclerite* (AX_3), situated in the posterior region of the wing-base, forms the basal support of the anal region. Anteriorly it is wedged in between the second axillary and the radio-median plate (RM), and postero-laterally it is connected with the anal basal area.

The *fourth axillary* (AX_4), situated lateral to the parascutellar lobes (PSCL), is a small roundish sclerite carrying a pair of posterior processes between which, as described above, projects the lateral prescutal process of the metanotum (Fig 31. PAA_3)

Anterior to the second axillary sclerite is situated the *costo-subcostal basal sclerite* (CSC) which proximally works against the socket-like concavity (Fig. 28. S) in the margin of the suralar process of the mesoprescutum (Fig. 28. SAA_2); (Fig. 42. SAA). In the anterior-most membrane of the wing-base is seen a small sclerite, the *tegula* (TG).

The base of the tegmen is supported from below by the *pleural wing-process* (Fig. 30. PWP_2) and three *epipleurites*, of which two, situated in front of the pleural process are known as the *basalars* (IBA_2, $2BA_2$), while the third situated behind is known as the *subalar* (SA_2). The basalars which lie free in the basal wing-membrane, support the ventral basal region of the costo-subcostal head as well as the side of the second axillary ($2AX_2$). The subalar (SA_2) has a dorsal notch into which projects a process of ventral root of the second axillary.

Basal region of the hind wings:—The *first axillary sclerite* (Fig. 43. AX_1) of the hind-wing is without any anterior neck-like prolongation; in other respects it resembles the first axillary of the tegminal base. Anteriorly it is connected with the anterior notal wing process (ANP) of the metathoracic scutum, by a ligamentous thickening of the chitin. Mesially it is applied to the margin of the posterior notal wing-process (PNP). Laterally it touches the inner margin of the second axillary (AX_2) with which it is movably hinged.

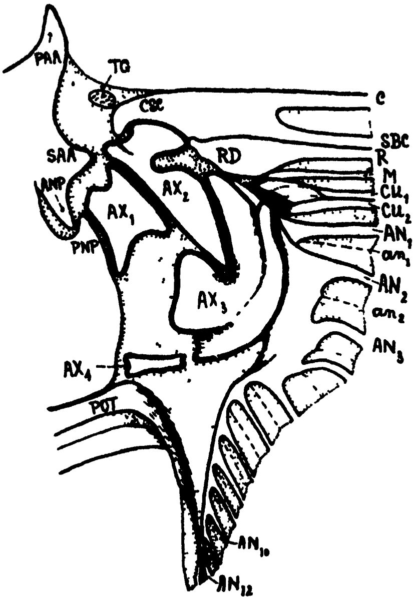


FIG. 43. Dorsal view of the *base of the hind wing* showing the wing sclerites. ×8.

AN—Convex anal vein. an—Concave anal. RD—Chitinised base of Radius. Other lettering as in Fig. 42.

The *second axillary* (AX_2) is a flat elongate sclerite attached anteriorly to the head of the costo-subcosta (CSC) and the radius (RD). Its tapering posterior end projects into a deep notch of the third axillary (AX_3).

The *third axillary sclerite* (AX_3) which is similar to the AX_3 of the tegmina in structure and position, is immovably attached to the anal basal region.

The *fourth axillary* (AX_4) is a small rod-like sclerite situated between the basal process of the third axillary and the lateral margin of the parascutal area of the metanotum.

The costo-subcostal head of the hind wing, which is bent posteriorly, is not directly connected with the tergal margin as in the case of the tegmina. In front of it is situated the tiny *tegula* (TG).

The *post-tergal* margin (POT) extends postero-laterally and sends a chitinised rod-like support to the posterior border of the anal base.

The base of the hind wing from below (Fig. 30) is supported by the *pleural wing-process* (PWP_3) and strengthened by the presence of two *basalars* and one *subalar*. The two basalars (IBA_1 ; $2BA_3$), rod-like in form and hinged to one another end to end, support the costo-subcostal region from below. Against the broadened head of the pleural wing-process rests the ventral side of the second axillary ($2AX_3$). The single subalar (SA_3) has a broad base and sends obliquely forward a narrow process which rests against the posterior margin of the second axillary.

SPIRACLES

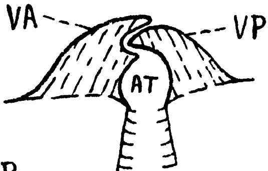
There are ten pairs of spiracles in *S.gregaria* of which two are thoracic and eight abdominal. Of the two thoracic pairs, the front one, which is *mesothoracic* in origin, is situated in the intersegmental region between the pro- and meso-pleuræ, nearer the anterior margin of the latter. The second pair, which is *metathoracic* in origin, lies in the postero-ventral corner of the meso-epimeron. The *abdominal* spiracles are situated in the antero-lateral corners of each tergite of the first eight abdominal segments.

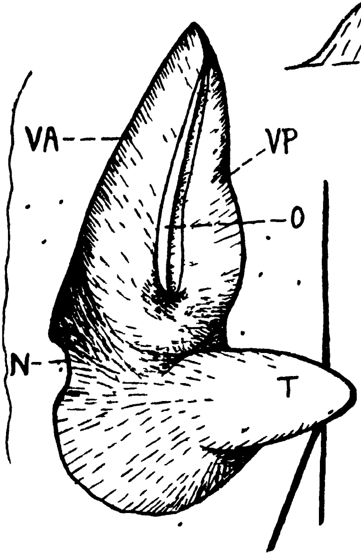
First thoracic spiracle :—(Figs. 30, 44, 45, 46. SP_2). It is the largest in size and is normally hidden under the lateral extension of the pronotum. It is surrounded by a chitinised area known as the *peritreme* which forms a pair of external lips, the *valves*, bounding the vertically elongate orifice of the spiracle. At the ventral end of the spiracular valves, the peritreme is strongly chitinised and sends off a posteriorly directed conical *process* (Fig. 44. T) which is hollow inside. This process which stands above the level of the spiracular valves, presumably serves "as a stop to prevent the covering flaps of the protergum from resting too closely against the spiracle" (Snodgrass, 1929). In the anterior margin of the peritremal area, there is a deep notch (N) with a corresponding internal process (Fig. 45. n), evidently for muscle-attachment.

Of the two spiracular *valves*, the anterior one (VA) is bigger, longer, and more raised than the posterior one (VP). It is strongly constituted and less movable, and has a deep longitudinal groove along its inner side parallel to the upper margin. The posterior valve, which is a freely-movable flap, is mainly concerned in the closing and opening of the spiracular orifice.

The vertically elongate *spiracular aperture*, (O) which is somewhat sinous in outline, measures 1 mm. in length in the female locust. It leads within into the *atrium* (Fig. 46. AT) from which are given off two tracheal trunks, a large antero-dorsal and a small postero-ventral (Fig. 45). The septum separating these two trunks sends forward a strongly chitinised *process* (P) which at its base is connected with the inner wall of the posterior valve.

The *opening* and *closing* of this spiracle is effected by means of a pair of muscle-bands, attached between *n* and *P*, and *n* and *Q* (Fig. 45). According to Snodgrass (1929) contraction of the (*Pn*) muscle pulls the upper margin of the posterior valve (VP) towards its longitudinal groove of the anterior valve, and thus closes the





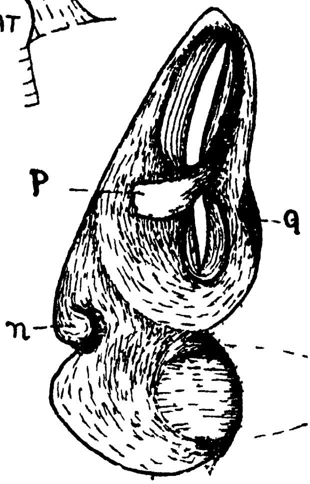


FIG. 44. (Left) *External* view of *mesothoracic spiracle.* ×30.

N—Notch in the peritremal margin. O—Spiracle-orifice. T—Peritremal process. VA—Anterior valve. VP—Posterior valve.

FIG. 45. (Right) *Internal* view of *mesothoracic spiracle.* ×30.

n—Process corresponding to N (Fig. 44). P—Process from the intertracheal septum. Q—Point of muscle attachment.

FIG. 46. (Top) Vertical *section* through mesothoracic spiracle (Diagrammatic).

AT—Atrium. VA—Anterior valve. VP—Posterior valve.

spiracle. Contraction of the *nQ* muscle works in the opposite direction resulting in the opening of the spiracle. Fig. 46 is a diagrammatic vertical section through the spiracle showing the relation of the two valves at their upper margins. Lee (1925) states that "the valvular lobes have a wax-like secretion and are perfectly airtight when closed."

The second thoracic spiracle:—(Figs. 30, 47, 48, 49). This spiracle is situated in the postero-ventral corner of the meso-epimeron (Fig. 30. SP_8), and is smaller in size than the first thoracic. Its elongate orifice measures ·8 mm. in length (♀), and is bounded by a pair of elongate, chitinised *valves* or lips. The posterior valve (VP) is slightly raised so as to overlap the upper edge of the anterior lip, when the spiracle gets closed. The ventral ends of both the valves are united to form a strongly chitinised area which internally gives rise to a small protuberance (Fig. 48. P_8). The *closing* and *opening* mechanism of this spiracle is

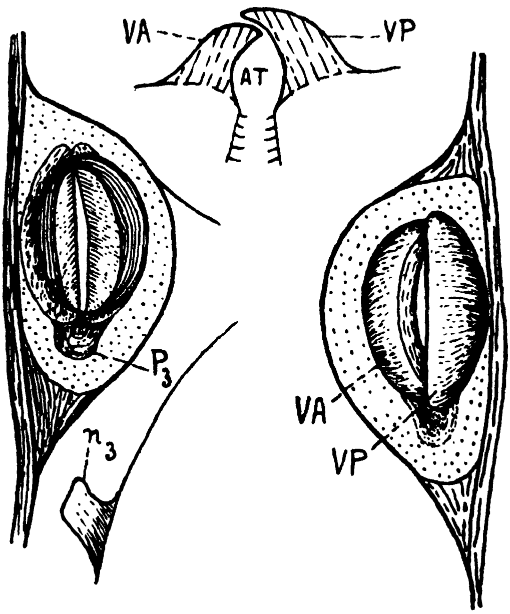


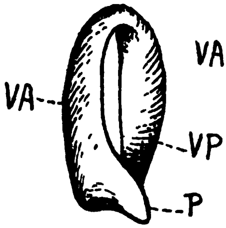
FIG. 47. (Right) *External* view of *metathoracic spiracle.* ×30.
Lettering as in Fig. 44.

FIG. 48. (Left) *Internal* view of metathoracic spiracle. ×30.
P—Process. n—Process from mesocoxal margin.

FIG. 49. (Top) Vertical *section* through metathoracic spiracle (Diagrammatic). Lettering as in Fig. 46.

worked by means of a muscle-band attached at one end to P_8 and at the other end to a process n_8 arising from the adjoining margin of the mesocoxal cavity. Contraction of the P_8—n_8 muscle results in the movement of both the valves towards one another, the anterior one passing under the posterior and thus closing the spiracular opening (Fig. 49). Relaxation of the same muscle results in the valves moving away from one another, thus opening the spiracular orifice.

Abdominal spiracles:—(Figs. 50, 51, 52. SP_1). Of the eight pairs of abdominal spiracles, the first one is located just anterior to the base of the laterally situated *tympanal organ* (TM) in the first abdominal segment. The rest are situated, as mentioned above, in the anterolateral corners of the abdominal tergites (Fig. 52. SP_2).



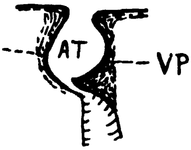


FIG. 50. (Left) *Internal* view of an *abdominal spiracle.* ×90.

P—Process. VA—Anterior valve. VP—Posterior valve.

FIG. 51. (Right) Vertical *section* through abdominal spiracle. (Diagrammatic). Lettering as in Fig. 46.

A typical abdominal spiracle consists of a small oval external orifice, about ·5 mm. in length (♀), on level with the body-surface. The slit leads within into the *atrium* (Fig. 51. AT), and is provided with a pair of chitinised *valves.* The anterior valve (VA), which is freely movable, has its ventral inner corner produced into a process (P) to which is attached the occlusor muscle of the spiracle. Contraction of this muscle pulls the base of the anterior valve over that of the posterior one, thus closing the passage from the atrium to the tracheal trunk (Fig. 51).

The abdominal spiracles differ from the thoracic ones in two respects: (i) There are no external protruding lips or valves as found in the case of the thoracic spiracles, and (ii) the closing mechanism of the abdominal spiracles is internal as contrasted with the external one of the thoracic spiracles.

With regard to the *function* of the various spiracles, Lee's (1925) experiments indicate that the thoracics and the first two abdominals are *inspiratory* in function, while the remaining abdominals are *expiratory*. It would however be worth while to repeat the experiments in the case of the desert locust and see if they hold good in this insect.

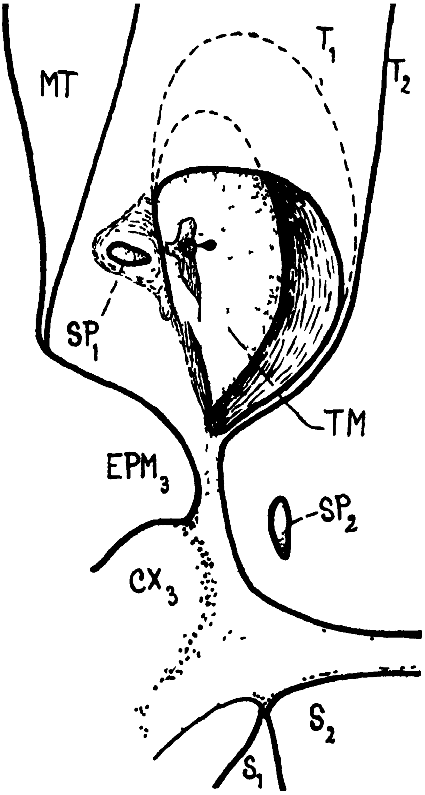


FIG. 52. Lateral view of first abdominal segment showing the location of *abdominal spiracle* and *tympanum*

CX—Metacoxal base. EPM—Metaepimeron. MT—Metatergum. S—Abdominal sternite. SP—Spiracle T—Abdominal tergite. TM—Tympanum.

(To be continued)

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II. ON THE NUMBER OF CHROMOSOMES OF SOME INDIAN ARACEÆ.

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INTRODUCTION

In a previous paper (Asana and Sutaria, 1935) we have recorded our observations on the morphology and number of the somatic and the male meiotic chromosomes in Arisæma Murrayi. On the chromosome number in Araceæ many detailed studies have not been made. The lists of chromosome numbers made by Gaiser (1926–33), Ishikawa (1916) and Tischler (1931 and 1935–36) include almost all the plants belonging to this group.

In the present study 7 species of plants belonging to 6 genera as mentioned below have been investigated. The identity of each species has been checked with the help of botanical descriptions given by Blatter and McCann (1931).

TABLE I.

Theriophonum minutum, Willd	$2n=16$.
Amorphophallus campanulatus, Roxb	$2n=26$.
„ silvaticus, Roxb	$2n=26$.
Colocasia esculanta, Linn	$2n=28$.
Spathiphyllum cannæfolium	$n=15$.
Zamioculcas Loddigesii, Decne	$2n=34$.
Aglaonema picta	$2n=40$.

MATERIAL AND METHOD

The material used in connection with this investigation was taken from cultivated and wild varieties of Aroids obtained from different centres in India, namely, Bombay, Surat, Agra, Saharanpur, Madras and Darjeeling.

Observations were made on root-tip cells for the somatic chromosomes and on pollen mother cells for the reduction division.

For the fixation of root-tips corms or tubers were carefully removed from pots and rinsed in water. Root-tips were cut with a safety razor blade and fixed in either Flemming, Navaschin (1% chromic acid 10 parts ; glacial acetic acid 1 part ; pure formalin 4 parts) or Lewitsky's fixative (5% chromic acid and 5% formalin in the proportion of 2 parts of the former to 8 parts of the latter). For flower buds Carnoy-Navaschin was exclusively used. This fixative gave somewhat varying results according to the peculiarities of the species and varieties on which it was used.

After fixation for 24 hours, the material was washed in running water overnight, dehydrated in gradually increasing grades of alcohol, cleared with Xylol, and embedded in 52° paraffin. Some material was dehydrated and cleared in Dioxane.

Sections were cut 12 microns thick for root-tips and 9 to 12 microns for pollen mother cells. They were exclusively stained with Heidenhain's iron alum hæmatoxylin.

OBSERVATIONS

THERIOPHONUM MINUTUM, WILLD.

The plants were obtained from Madras and cultivated in the College garden. The morphology of Aroid chromosomes depends mainly upon two factors, their length and the position of their spindle fibre attachments. The somatic complement of T. minutum consists of 16 fairly large chromosomes showing little variation in size (Fig. 1). Some have a sub-median attachment which forms J-shaped chromosomes; while most of them are more or less V-shaped due to the median fibre attachments. Fig. 2 represents a polar view of the somatic metaphase of the same plant from the material fixed in Navaschin's fluid. By comparing this figure with Fig. 1 it will be clearly seen that chromosomes swell considerably due to the large percentage of acetic acid in the Navaschin's fixative, whereas they remain slender and maintain more or less their natural form when the material is fixed in Lewitsky as seen in Fig. 1. This is the first record regarding the number of chromosomes in this plant. Fig. 3 represents a tangential view of the somatic anaphase of the same plant. Here some of the chromosomes show distinct constrictions.

AMORPHOPHALLUS CAMPANULATUS, ROXB.

It is one of the common cultivated Aroids of Gujarat. The somatic number of chromosomes of this species was counted to be twenty-six (Fig. 4). This agrees with the results obtained by Nakajima (1933) and Takahashi as reported by Kihara, Yamamoto and Hosono (1931) in A. Konjak in which there are n=13 chromosomes. The chromosomes are large and do not vary much in length. They are either rod-like, J-shaped, or V-shaped. Fig. 5 represents a polar view of the somatic anaphase where all 26 chromosomes are quite distinct and can be easily counted.

AMORPHOPHALLUS SILVATICUS, ROXB.

A few corms of this plant were obtained from Madras. According to Blatter and McCann (1931) the plants are very common in N. Kanara and the Nilgiris. The somatic complement consists of 26 large chromosomes mostly with sub-median and median insertions. The chromosomes are slightly larger than those of A. campanulatus. The long rod-shaped chromosomes do not show any secondary constrictions.

COLOCASIA ESCULANTA, LINN.

It is one of the commonest of Aroids cultivated for its edible corms and leaves throughout the whole of India. Blatter and McCann (1931) in their revision of the flora of the Bombay Presidency have named the plant C. esculanta and not C. antiquorum as it is commonly known. There are two distinct varieties—one with big fleshy corms with dark purple leaves and stalks and the other with small elongated corms in which leaves and stalks are green.

In both these varieties the somatic chromosomes are 28 in number. Fig. 7 shows the chromosomes of the big variety. The chromosomes vary in size and are either rod-like, J– or V–shaped. In the small variety (Fig. 8) the chromosomes show considerable variation in size and have clear constrictions. Most of the chromosomes are subterminally inserted.

According to Maeda (1932) there are 14 haploid chromosomes in both C. antiquorum and C. gigantea. This is in accord with our count of 28 diploid chromosomes in the root-tips of our material. It is interesting to note that in contrast to our observations and those of Maeda (1932), Nakajima (1933) gives 21 as the haploid chromosome number in C. antiquorum. This disparity in observations can only be explained on the assumption that either the Japanese or the Indian form of C. antiquorum has been wrongly identified, or the one or the other is a variety of the type species in view of the fact that the numbers 21 and 28 are the multiples of the assumed basic number 7.

SPATHIPHYLLUM CANNÆFOLIUM.

It is a common garden Aroid and was obtained from Bombay.

Owing to the scarcity of root-tip material, the somatic chromosome number was not determined. Fig. 9 represents a polar view of the heterotypic metaphase. The 15 bivalents of the complement are very irregular in shape. They also vary in size. One pair of chromosomes has a distinct satellite. Matsuura and Sutô (1935) have also recorded the presence of chromosomes with a satellite in Philodendron Andreanum. Fig. 10 shows in side view 15 chromosomes in a homœotypic metaphase where the chromosomes are very irregular in shape. This lobed appearance is a very conspicuous feature in the morphology of the chromosomes in this plant. In several cases in the polar views of both the heterotypic metaphase and anaphase (Fig. 11) a pair of satellite bearing chromosomes is distinctly in evidence.

With regard to the number of chromosomes in this species it may be noted that Jussen as reported by Tischler (1931) has observed that the haploid number in S. Patinii is only 9. This present finding, n=15, adds, therefore, a new chromosome number to this genus.

ZAMIOCULCAS LODDIGESII, DECNE.

These plants were obtained from Saharanpur. The somatic complement consists of 34 large chromosomes having median or submedian insertions (Fig. 12). The chromosomes vary in size. Those which are rod-like among them have constrictions in the middle. This is the first record regarding the number of chromosomes in this plant.

AGLAONEMA PICTA.

The number of somatic chromosomes in A. picta is 40 (Fig. 13). According to Gow (1908 and 1913) there are only 8 haploid chromosomes in A. versicolor. The chromosomes vary greatly in size. A. picta is obviously a polyploid species.

SUMMARY

1. This paper represents the results of a cytological study from root-tips and pollen mother cell preparations of 7 species of Aroids.
2. The chromosome numbers in Theriophonum minutum, Amorphophallus silvaticus, Spathiphyllum cannæfolium, Zamioculcas Loddigesii and Aglaonema picta are recorded for the first time.
3. In Spathiphyllum cannæfolium a pair of chromosomes bears a clear satellite.

ACKNOWLEDGMENT

The work described in this paper has been faciliated by a grant received by the Junior author from the University of Bombay, for which the authors express their sincere appreciation.

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EXPLANATION OF PLATES.

Drawings were made with the aid of the Abbe camera lucida at stage level. All figures were drawn under a 2 mm. oil immersion Zeiss apochromatic lens (N A. 1.40) with Zeiss compensating ocular 20X. Figures reproduced without reduction.

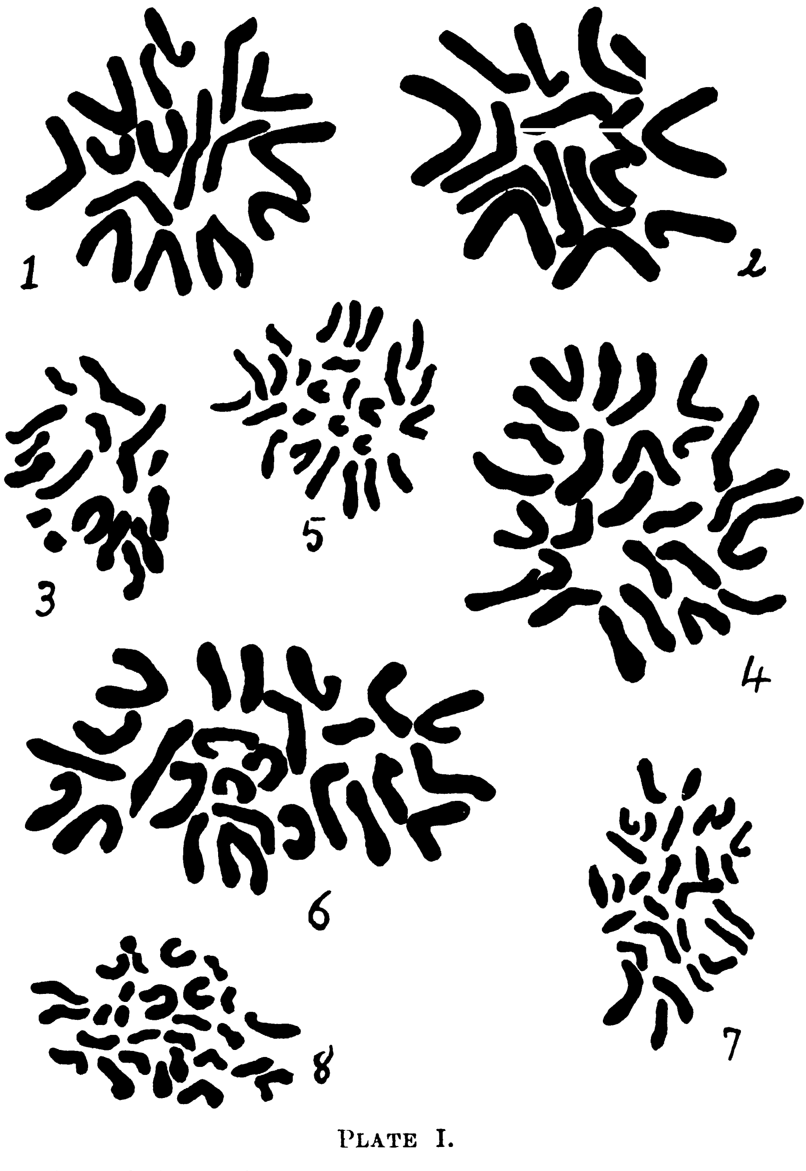

PLATE I.

FIGS. 1, 2, 4, 6–8. Somatic chromosomes of various Aroids, drawn from root-tip cells in the metaphase and Figs. 3 and 5 anaphase of mitotic division, polar view.

Fig. 1. Sixteen chromosomes of Theriophonum minutum (Lewitsky).
Fig. 2. 2 n = 16 T. minutum (Navaschin).
Fig. 3. 2 n = 16 (anaphase) T. minutum.
Fig. 4. Twenty-six chromosomes of Amorphophallus campanulatus.
Fig. 5. 2 n = 26 (anaphase). A campanulatus.
Fig. 6. 2 n = 26 A. silvaticus.
Fig. 7. Twenty-eight chromosomes of Colocasia esculanta (large variety)
Fig. 8. 2 n = 28 C. esculanta (small variety).

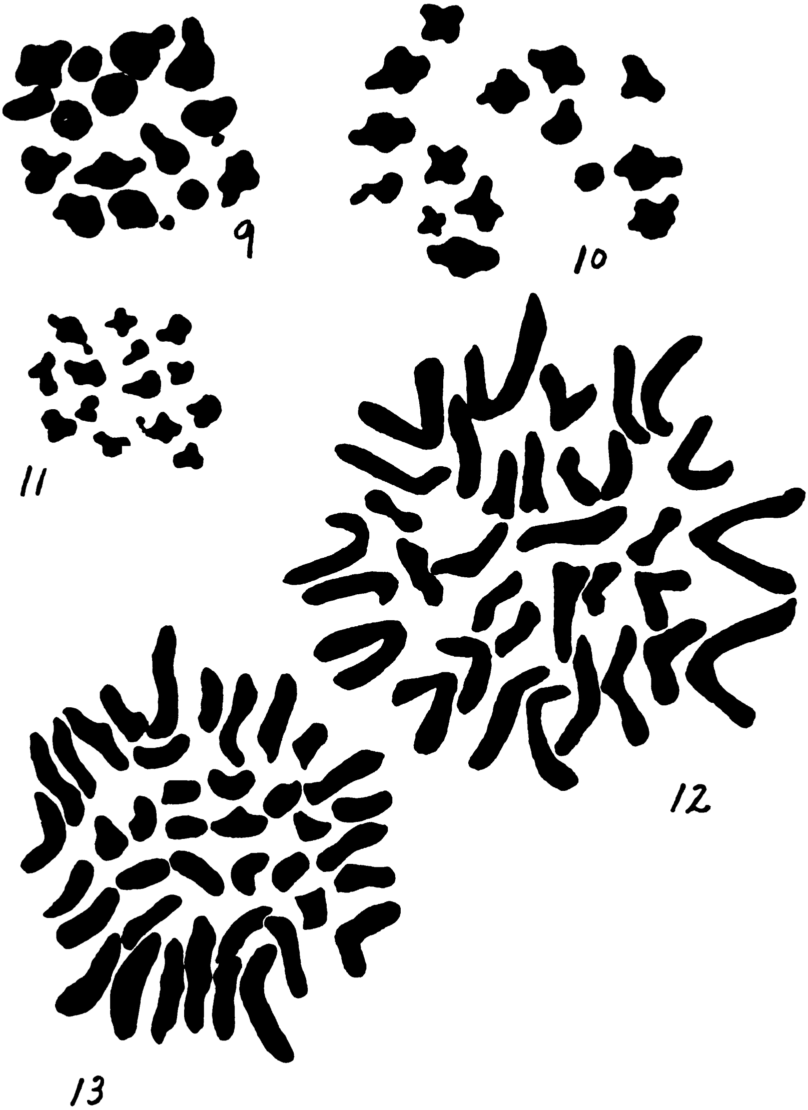

PLATE II.

Fig. 9. Polar view of fifteen chromosomes (one pair with a satellite) of the heterotypic metaphase from P. M. C. of Spathiphyllum cannæfolium.

Fig. 10. n = 15 homœotypic metaphase of S. cannæfolium.

Fig. 11. n = 15 heterotypic anaphase (one pair with a satellite) of S. cannæfolium.

Fig. 12. Polar view of thirty-four diploid metaphase chromosomes from the root-tip cells of Zamioculcas Loddigesii.

Fig. 13. Polar view of forty diploid metaphase chromosomes from the root-tip cells of Aglaonema picta.

VARIATIONS IN THE LEAVES OF THESPESIA POPULNEA, *SOLAND.*

(N. O. MALVACEAE,)

By

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Thespesia populnea, *Soland* is a semi-mangrove, which is often found growing wild along sea-shores. It also occurs inland, where it is chiefly planted as a road side tree and for the economic value of its wood. Different forms of leaves which are described below were first noticed and collected from a road side tree at the Northeast of Bombay. Similar forms of leaves were also noticed subsequently on most of the trees growing in the same locality and elsewhere and it appears from the large number of observations made throughout the last two years that, it is a common phenomenon with the plant to bear these different types of leaves, of course numerically very few in comparison to the number of the normal ones, irrespective of season and locality.

NORMAL LEAVES (1)

Leaves 3—8 inches long, broadly ovate, cordate, acuminate, entire and both the surfaces almost smooth when old, but covered with silky pubescence when young; ptyxis conduplicate; finely reticulately veined with five to seven prominent nerves arising from the top of the petiole. The mid-rib is rather stronger and more prominent than the other two or three pairs of lateral veins, which are symmetrically arranged on either side of the mid-rib; the basal lateral vein being thinner than the one above it; petioles 2—5 inches long.

Besides these normal leaves there are found almost on all plants about ten different forms of leaves which are described below and shown in Plate 1, A—J.

There are a number of leaves, which are ovate or cordate with obtuse apex instead of the normal acuminate (Plate 1, B).

There are some which are reniform with either rounded or retuse or emarginate apices. (Plate 1, C, D & E.)

Then there are some which are forked and bilobed as seen in Bauhinia. The degree of fission varies in different leaves. All the stages between partial fission and almost complete division into two distinct leaflets are met with. (Plate 1, F & G).

There are some which are oblique, one half being greater than the other; apex may be acute or obtuse (Plate 1, H).

Like the trilobed leaves of Thespesia macrophylla, *Blume* some leaves showed a tendency of developing lobes. Only one lobe is found well developed on the greater half of the oblique leaf (Plate 1, I), while the other smaller half showed just a small outgrowth (Plate 1, J), thus indicating its tendency to become trilobed.

EXPLANATION

The possible explanation as to the occurence of these different forms of leaves may be as under :—

It can be seen from a number of observations that these different configurations are present from the very inception of these leaves. The probable cause of this diversity is in my opinion due to some pathogenic condition set up in the meristematic cells by the invasion of the leaf primordium by some pathogenic micro-organisms, which can be seen when the leaf structure is microscopically examined.

In the normal course of the development of the leaf the growth in surface extent proceeds from above downwards, at first nearly uniform and later on chiefly at the margins. This assumption is based upon the divergent course of the veins, which is the result of the basipetal development of the leaf, the mid-rib being comparatively stronger than the lateral one and the first to appear. The weakest lateral vein at ·the base of the lamina appears last. The development of the leaf with obtuse apex (Plate 1, B) may be due to the arrest of the actual meristematic tissue or may be due to the death of the cells differentiated from it at the apex of the leaf at some time in its development before the mature growth form is attained. If the infection takes place a little earlier or if it is stronger and very active and if the protective tissue, the cicatrice, is developed a little later, then we get either a leaf with retuse apex (Plate 1, D) or one with emarginate apex (Plate 1, E). In the case where the marginal growth is more than the apical, then we get a kidney-shaped leaf (Plate I, C). In the case of bilobed leaves (Plate 1. F & G) and others with varying degree of fission the apical meristem dies very early and the tissues lying close to the main axis only develop. Similar types of bilobed or forked leaves were observed in Anacardium occidentale, L. and in one of the cotyledons of Michelia

Champaca, L. by Sabnis (3); Aralia Guilfuylei, by Saran (4) and Mirabilis jalapa, Linn. by Singh. In the case of Aralia no explanation is given as to the cause. In Mirabilis, what Singh (5) explains as fasciation seems to be an instance of forking. However in the first two cases it is the main axis of the epipodium *i. e.* the mid-rib which instead of growing continuously, forks into two and each of these daughter axes gives rise to tertiary branches which develop winged expansions. Thus each forked vein develops a separate lobe of its own. The degree of fission depends upon the point where forking takes place. Such is not the case in the present instance, where the mid-rib does not bifurcate but end abruptly. The oblique leaf (Plate 1, H) is due to the difference in the rate of growth along the sides of the mid-rib. This unequal growth can be noticed even when the leaf is in the bud condition and as the asymmetry appears very early, in fact from its inception, it cannot be said that this difference in growth is brought about by some external factor like light later on. This unilateral growth may be the result of either lateral pressure while in the bud condition or may be due to some disturbances in the physiology of the growth of the leaf. The latter is more probable than the former. The occurence of the lobed leaves (Plate 1, I & J) like its allied species Thespesia macrophylla, Blume, can also be ascribed to unequal growth and may suggest phylogenetic relationship.

In conclusion it may be said that the different configurations of the leaves are neither due to reversion to the juvenile form as no such leaves occur during its life cycle as observed by germinating seeds in the Institute garden and in natural habitat, nor it is due to tip-burn as found in Potato, nor to hopper-burn, a trouble which appears to be connected with the work of leaf hoppers (2) They may be due to arrest or death brought about by micro-organisms as can be seen from the internal structure. This arrest or death may take place earlier and consequently the construction of the arrested leaves varies in an extraordinary degree.

SUMMARY.

Observations were carried out on the different configuration of the leaves of Thespesia populnea, *Soland*, and it has been suggested that these differences in outline may be due to pathological condition brought about by micro-organisms which disturb the vital activity of the growing leaves.

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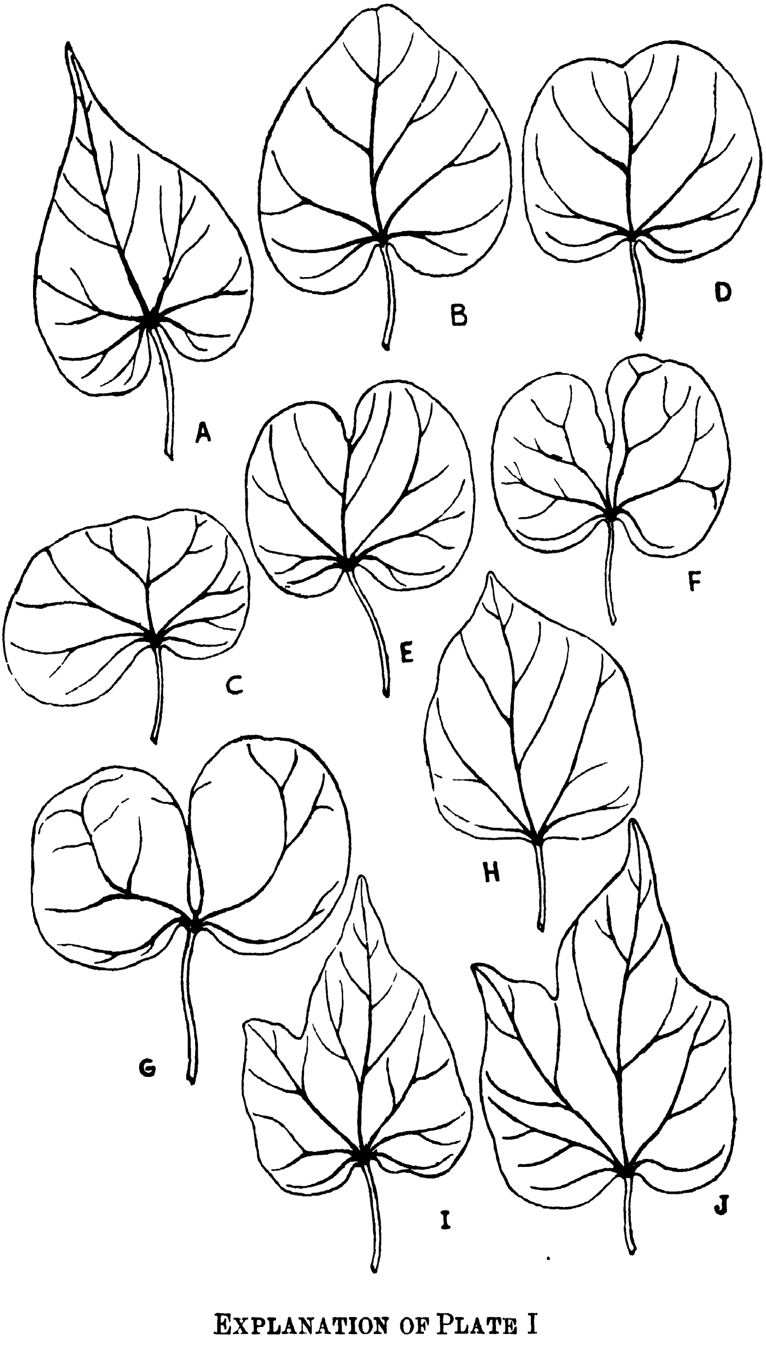

Explanation of Plate I

A. Normal Leaf; B. Cordate leaf with obtuse apex; C. Reniform leaf with rounded apex; D. Reniform leaf with retuse apex; E. Reniform leaf with emarginate apex; F & G; Bilobed leaves; I. & J. Lobed leaves.

HISTOLOGICAL STUDIES OF THE DIGESTIVE SYSTEM OF THRIPS.

(With 22 Text-figures)

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INTRODUCTION

Recent work on the problem of the transmission of Plant Viruses shows that juice-sucking insects, particularly Thrips and Aphids, act as vectors of plant viruses. But a review of the previous work on these insects points out that very little information is known so far on the histological details of the alimentary canal of an insect belonging to either of these groups. It is thought, therefore, that a detailed study of the digestive tract may be of considerable help in elucidating many points in connection with the changes brought about in its structure by the effects of the activity of the viruses. It is with this object in view of affording a ground-plan for future comparative study that the present investigation of the digestive tracts of the two species of Thrips, *viz. Taeniothrips brunneicornis* (Bagnall) and *Scirtothrips dorsalis* (Hood) was undertaken.

MATERIAL AND TECHNIQUE

Specimens of *T. brunneicornis* and *S. dorsalis* were collected in the immediate vicinity of the Royal Institute of Science, Bombay, and in the farms attached to the Entomological Section of the Agricultural College, Poona, during the month of September in the years 1935-37.

The fresh and preserved insects were dissected in normal saline solution, glycerine, 70% alcohol, and oil of cloves. Different fixatives were tried, but Carl's aceto-formol and Carnoy's fluid alone gave excellent results.

In cutting serial sections of the whole insect, the chloroform-paraffin method was adopted. Mixture of soft (58°C) and hard (68°C) paraffins, in the proportion of 3 : 1 was used for embedding. The sections were stained with Ehrlich's and Delafield's hæmatoxylin with eosin and Orange G. as counter stains. Differentiation was carried out as usual in acid alcohol, but the method of differentiation in 1% aqueous solution of citric acid adopted by G.E. Newell and E.W. Baxter (1936) was also tried and found to yield more optical brilliance and better differentiation. But as the aqueous solution does not last long, the alcoholic solution of citric acid (1% in 70% alcohol) was used and found to give equally good results.

The drawings illustrating this paper were made with the help of the Abbe Camera lucida.

GROSS ANATOMY OF THE DIGESTIVE CANALS

The alimentary canal of *T. brunneicornis* (Fig. 1) (found on rose plants) is a looped tube (3 mm.) about twice the length of the insect. Like the typical gut of an insect it is divisible into three main parts : the fore-gut, the mid-gut and the hind-gut, of which the second division is the longest in this species.

FORE-GUT:—The fore-gut which is 1/6th the length (0.5 mm.) of the whole alimentary canal, consists of the chitinous pharynx, the thin tubular oesophagus, and the oesophageal valve which projects into the anterior end of the mid-gut. The pharynx is distinguished from the oesophagus by its larger diameter, together with differences in the chitinous intima and the muscular sheath. At intervals long dilator muscles are inserted on its dorsal wall. It is enclosed in a short, dark-brown, heavily chitinized chamber (Fig. 2) the *cibarium*, situated in the head-cavity. It is the food-pocket of the pre-oral cavity between the base of the hypopharynx and the under-surface of the clypeus; its external aperture

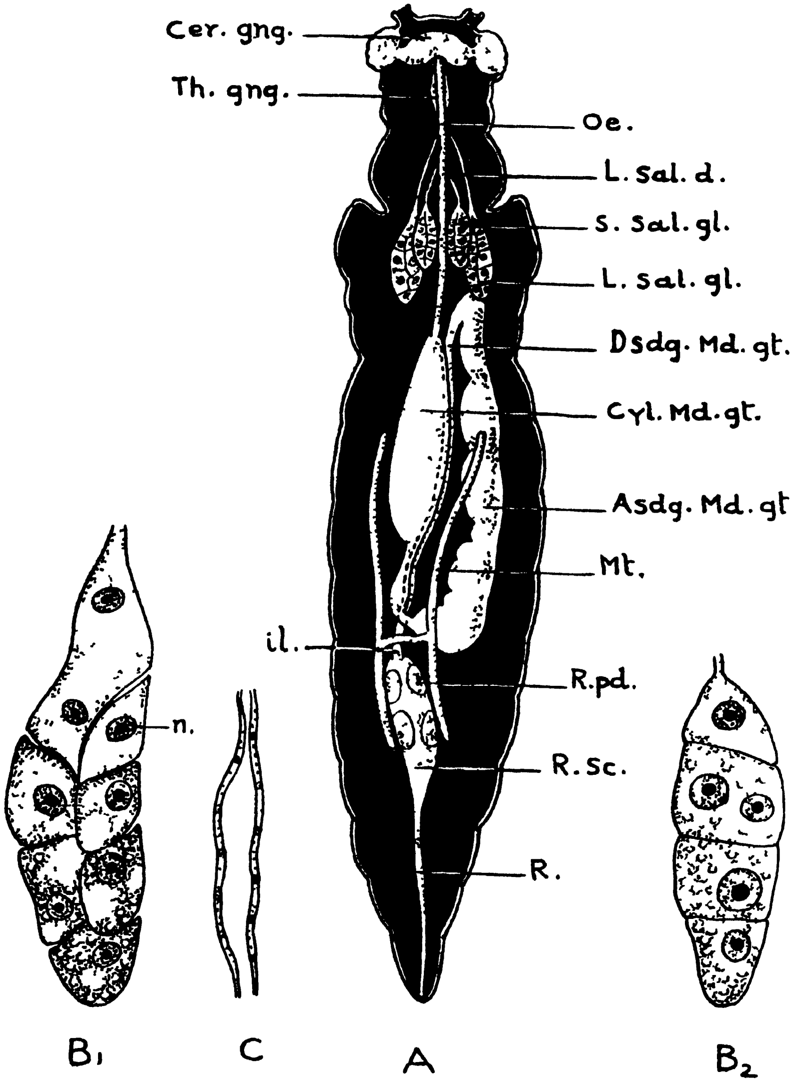

FIG. 1.

(A) Digestive system of *T. brunneicornis* showing alimentary canal, salivary glands, malpighian tubes and rectal pads. (8 × 10).

(B_1 and B_2) L.S. of the longer and shorter salivary glands respectively. (40 × 10).

(C) L.S. through the dilated region of the duct of a longer salivary gland. (40 × 10).

Asdg. Md. gt.—Ascending limb of the mid-gut; Cer. gng.—Cerebral ganglia; Cyl. Md. gt.—Cylindrical mid-gut; Dsdg. Md. gt.—De-cending limb of the mid-gut; il.—Ileum; L. Sal. d.—Duct of the longer salivary gland; L. Sal. gl.—Longer salivary gland; Mt.—Malpighian tube; n. Nucleus; R.—Rectum: R. pd—Rectal pad; R. sc.—Rectal sac; S. Sal. gl.—Shorter salivary gland; Th. gng.—Thoracic ganglion.

including that of the food meatus is the functional mouth. It is concerned with the suction of juices and is homologous with the pharynx of sucking insects. One may however distinguish it into two regions: a small, chitinized tube surrounding anteriorly the food meatus (f. m.) of the beak, and a widened and heavily

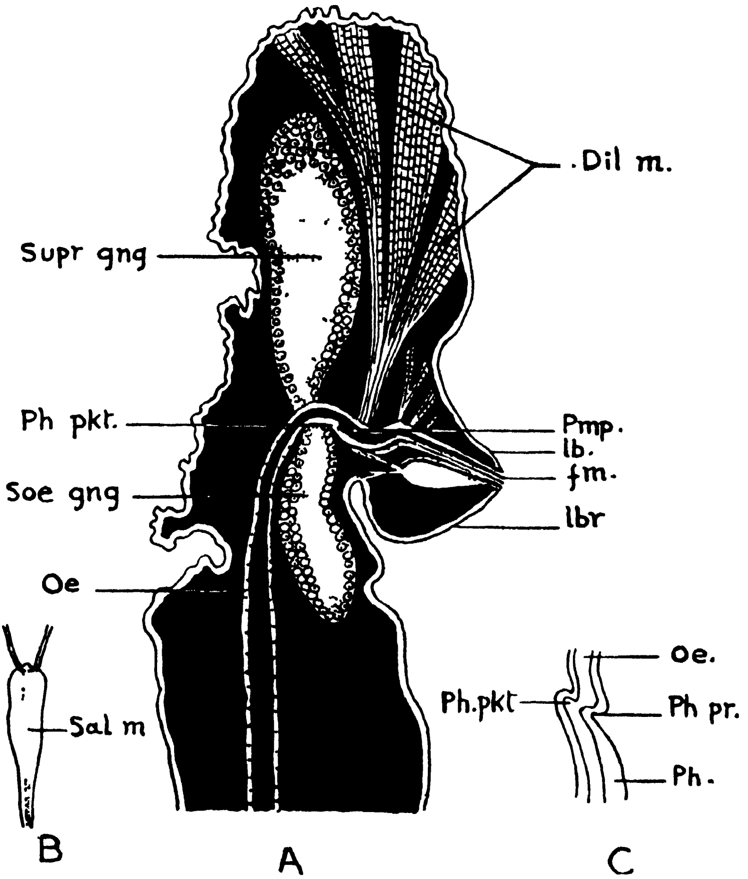

FIG. 2.

(A) Sagittal section through the head and pro-thorax of *T. brunneicornis* showing the food-meatus and sucking pump. (95 × 5).

(B) "Y" shaped chitinous piece.

(C) Pharyngo-oesophageal valve.

Dil. m. – Dilator muscles of pharynx; f. m. – Food meatus; lb. – Labium; lbr. – Labrum; Oe. – Oesophagus; Ph. pkt. – Pharyngeal pocket; Ph.pr. – Pharyngeal projection; Pmp. – Sucking pump; Sal m. – Salivary meatus; Soe. gng – Sub-oesophageal ganglion; Supr. gng. – Supra-oesophageal ganglia.

chitinized basal piece. There is a centrally located canal starting with the food meatus and continued backwards into the lumen of the oesophagus (oe.). The large dilator muscles (dil.m.) of the pharynx are inserted on its dorsal wall and have their origin on the anterior part of the facial region of the head. In addition to these, a number of short muscles arise on the clypeus and extend dorsally. These muscles contract and dilate the lumen of the cibarium, so that a vacuum is produced in the wake of which the juice is sucked up into this cavity. On the relaxation of the dilating muscles, the liquid food is forced through the valve situated at the postero-dorsal end of the pharynx into the oesophagus.

A valve-like fold (Fig. 2 C. Ph. pr.) cuts off the lumen of the oesophagus from the pharyngeal region. It is a prominent projection extending into the lumen from the postero-dorsal end of the pharynx and fitting into a pocket (Ph.pkt.) on the opposite side. Normally this valve is closed and consequently the lumen of the oesophagus is cut off from the pharynx.

OESOPHAGUS. In a freshly dissected specimen the oesophagus appears as a grey, semi-transparent tube with comparatively thick walls surrounding the lumen. It starts (Fig. 2) from the postero-dorsal end of the pharynx, and passes through the circum-oesophageal nerve ring and extends postero-medially above the sub-oesophageal and the thoracic ganglia. The oesophagus is merely the narrow posteriormost part of the fore-gut and serves mainly as a passage for food.

OESOPHAGEAL VALVE. At the junction of the oesophagus with the mid-gut is situated the oesophageal valve (Fig. 8). It consists of a double fold of the oesophageal wall projecting within the anterior end of the mid-gut and meant essentially for preventing the return flow of the liquid food from the mid-gut.

MID-GUT. The mid-gut is the longest part (2 mm.) of the alimentary canal and forms a loop in the body-cavity as shown in Fig. 1. It is divisible into two distinct regions, a proximal dilated and cylindrical chamber (Cyl. Md. gt.) and a distal bent portion consisting of the *ascending* (Asdg.Md.gt.) and *descending* limbs (Dsdg.Md.gt.). The former runs behind almost in a straight line extending upto the fourth visible sternite of the abdomen. It is usually gorged with plant-juices and is commonly known as the *stomach*. It measures about 0.6 mm. in length.

The narrow hind end of the stomach is sharply bent forward and continues on its right side as the *ascending limb* of the distal region. This limb runs forward upto the third thoracic segment where it bends backward and continues as the narrow, straight *descending* limb lying parallel to and in close contact with the right side of the stomach. It now runs beneath the hind end of the latter where the mid-gut passes into the hind-gut, the junction of the two being marked by the origin of four malpighian tubes. The ascending and descending limbs are of about the same length (O. 65 mm.), but the latter has a narrow calibre.

HIND--GUT. The hind-gut is very short (0.5 mm.) and goes straight to the anus. It is dilated in the beginning to form a rectal region. The hind-gut of this insect is divisible into a short ileum (il) and a long rectum (R) on account of a definite constriction between them. The ileum narrows posteriorly and projects into the rectum in the form of the rectal valve.

The anterior part of the rectum is dilated into a distinct, wide, pyriform structure, the *rectal sac* (R.Sc.) (120 μ wide). Its posterior part is a straight narrow tube often called the *rectum proper* (R). The wall of the rectal sac is thin and carries four oval thick rectal pads (R.pd.) projecting inwards and dimly visible from outside. It is at these places that the wall of the rectum is thickened and heavily chitinized.

In other species of thrips the hind-gut has been differentiated into two or three well defined regions. Uzel (1895) in *Aeliothrips fasciatus* finds the hind-gut divided into a small and a large intestine. Buffa (1898) divided the hind-gut of *Heliothrips hæmorrhoidalis*, on the basis of the presence of the rectal glands, into (1) a pre-glandular part, (2) a glandular part and (3) a post-glandular part. Moreover Klocke (1926) found in support of this division the presence of definite ring muscles between the pre-glandular and glandular parts in *Thrips physopus*. Jordan (1888) and Cary (1902), however, did not find any homologous structures in *Heliothrips dracænæ* and *Anaphothrips striata* respectively.

It is obvious from the above account that the ileum, the rectal sac and the rectum proper correspond to the pre-glandular, the glandular, and the post-glandular parts respectively as mentioned by Buffa.

THE DIGESTIVE CANAL OF SCIRTOTHRIPS DORSALIS.

The alimentary canal of the Chillie-thrips *(Scirtothrips dorsalis)* (Fig. 3) is a straight tube, almost as long as the body (2 mm.) and much shorter than the looped type found in *Tæniothrips brunneicornis.*

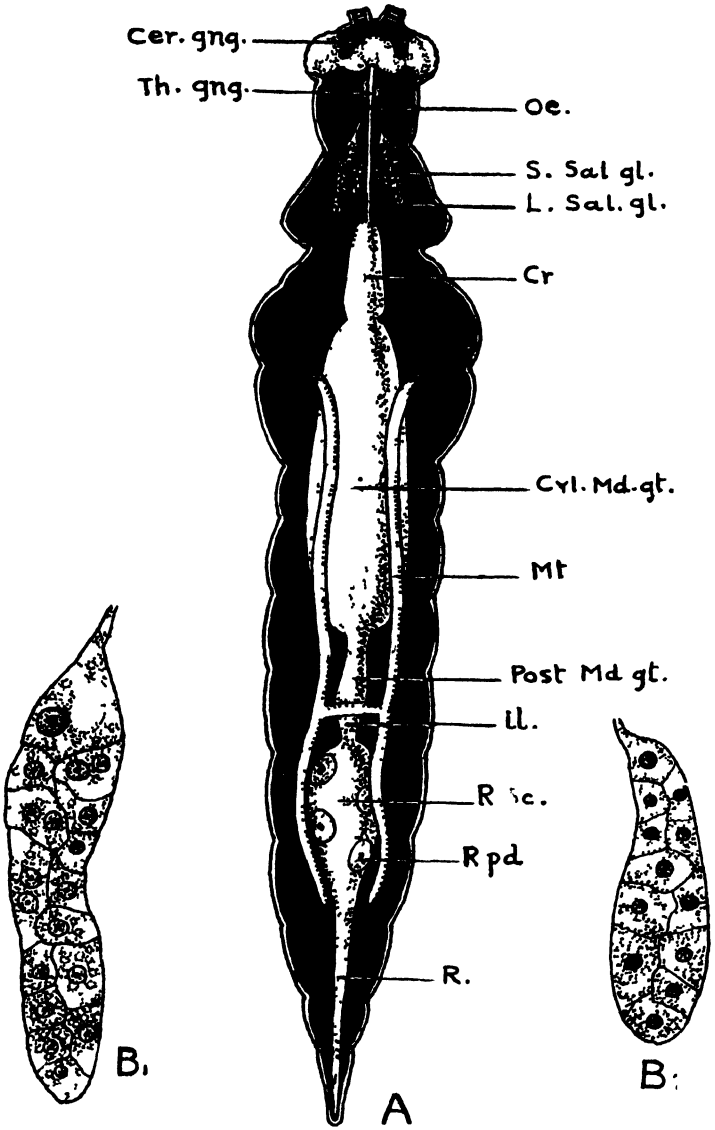

FIG. 3.

Digestive system of *Scirtothrips dorsalis* showing (A) alimentary canal, salivary glands, malpighian tubes and the rectal pads (8 × 10).

(B_1 and B_2) L. S. of the longer and shorter salivary glands respectively (40 × 10).

Cer. gng — Cerebral ganglion; Cr. — Crop; Cyl. Md. gt — Cylindrical mid-gut; il — Ileum; L. Sal. gl — Longer Salivary gland; Mt. — Malpighian tube; Oe. — Oesophagus; Post. Md. gt. — Posterior mid-gut; R. — Rectum; R pd — Rectal pad; R Sc. — Rectal sac; S. sal. gl. — Shorter salivary gland; Th. gan. — Thoracic ganglionic mass.

The fore-gut which measures about 0.6 mm. in length in this insect is formed of a short, broad tube extending upto the end of the second thoracic segment. The oesophagus (œ) at its posterior end is swollen to form the crop (cr.) which is usually absent in juice-sucking insects.

The oesophageal valve which is conspicuously seen in the Rose-thrips is absent here, and the fore-gut and the mid-gut are separated simply by a deep constriction. The constricted portion may be taken to represent the proventriculus of other insects.

The mid-gut forms nearly the middle third of the gut (0.8 mm.) in length. It is a straight wide chamber (0.62 mm.) (Cyl. Md. gt.) resembling the dilated stomach of *Tœniothrips brunneicornis.*

The hind-gut (0.7 mm. in length) is short and its beginning is marked by the insertion of malpighian tubes (Mt.). As in *Tœniothrips brunneicornis* it is similarly divisible into the ileum (il) and the rectum (R) with its rectal sac (R. Sc.) (0.125 mm. wide). The ileum is broader proximally and slightly tubular distally. The rectal valve of the former is also present in this species. The rectal pads are similarly situated but are more rounded than those of the Rose-thrips.

The four malpighian tubes (Mt.) of this species resemble in size, shape and connection those of *Tœniothrips brunneicornis.*

HISTOLOGY OF THE DIGESTIVE ORGANS.

(A) FORE-GUT. The walls of the different parts of the fore-gut show the same plan of arrangement of their different layers and the variation found in them relates to the folding of chitinous lining and to the relative disposition of the muscular layers. The character of the epithelium remains almost the same throughout the fore-gut. The cell boundaries are often indistinct and the chitinous lining relatively thick. The epithelium and the intima are thrown into longitudinal folds which allow for the expansion of the lumen as the latter becomes filled with liquid food. The cytoplasm of the cells is non-granular and the nuclei well-developed, each nucleus containing generally a single deeply staining nucleolus.

PHARYNX. In transverse sections of Rose- and chillie-thrips passing through the pharynx (Fig. 4), one sees, projecting into the lumen of the pharynx, six to eight longitudinal folds of chitin with an underlying layer of epithelium (Epth.). The ‘chitinous intima (C. int.) is seen here in a well developed condition. The outlines of these folds are irregular and wavy.

Since the cell boundaries are not clearly visible, the exact shape and size of each epithelial cell cannot be demarked. The cytoplasm of the cell is non-granular. A distinct ovoid nucleus (n) is seen at the apex of each fold in the section.

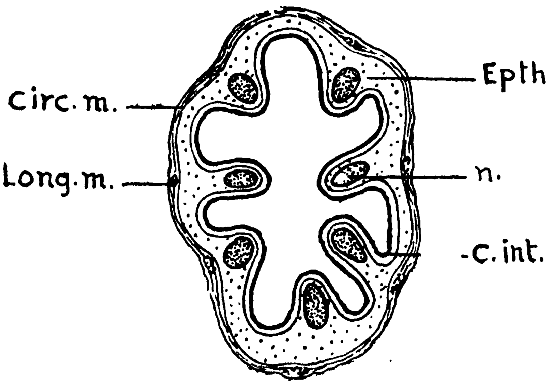

FIG. 4.

T. S. of the pharynx of *T. brunneicornis* (95 × 15)

C. int. – Chitinous intima ; Circ. m. – Circular muscles ; Epth. – Epithelium ; Long. m. – Longitudinal muscles ; n. – nucleus ;

The basement membrane on which the epithelium rests, is quite thin and cannot be easily distinguished from the surrounding muscular layer.

The musculature of this region consists of an outer layer of circular fibres (Circ. m.), and a relatively thin, broken inner layer of longitudinal muscle fibres (Long.m.). The former is so thick that the muscular coat in this region appears to be made by it alone. The longitudinal muscle fibres are arranged in bands extending along the external shallow grooves opposite the internal folds.

OESOPHAGUS. In a transverse section of the oesophagus (Fig. 5) of the Rose-thrips, only four folds of the intima are

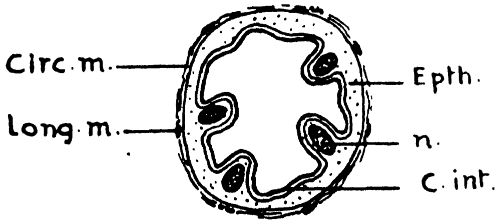

FIG. 5.

T. S. of the oesophagus of *T. brunneicornis* (95 × 15)

C. int. – Chitinous intima ; Circ. m. – Circular muscles ; Epth. - Epithelium ; Long. m. – Longitudinal muscles ; n. – Nucleus.

visible, the remaining folds of the pharynx having been flattened out. The epithelium (Epth) is similarly raised up and the boundaries of the epithelial cells are likewise indistinct, but the nuclei are small, staining deeply with hæmatoxylin. The chitin (C. int.), however, becomes weaker and less compact. In the region of the pharynx the chitin is distinctly yellow, presumably owing to its thickness, but it is almost colourless and transparent in the oesophageal area. Underlying the epithelium is the basement membrane which merges into the layer of circular muscles (Circ.m.). The latter, unlike those of the pharynx, are moderately developed. The longitudinal muscles (Long. m.) are also poorly developed. They consist of a few narrow strands lying scattered on the surface of the oesophagus. Owing to its extreme thinness, the peritoneal lining covering the external surface of the muscularis can hardly be distinguished from it.

The general epithelial lining of the oesophagus in the Chillie-thrips (Fig. 6) is not thrown into large folds as in the Rose-thrips. A large rounded nucleus (n.), is clearly seen at the apex of each fold. The boundaries of the epithelial cells (Epth.) are indistinct, and in the clear cytoplasm a few granules are irregularly distributed. The intima (C. int.) is seen here as a fine thread-like outline closely investing the epithelial cells. The musculature is poorly developed. The peritoneal lining cannot be distinguished as a separate layer from the muscularis.

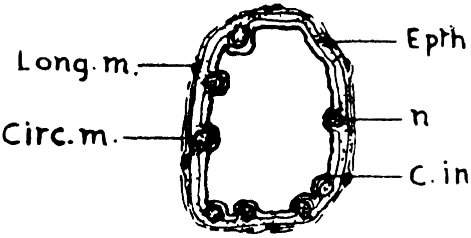

FIG. 6.

T. S. of the oesophagus of *S. dorsalis* (95 × 7)

C. int. – Chitinous intima; Circ. m. – Circular muscles; Epth. – Epithelium ; Long.m. – Longitudinal muscles; n. – Nucleus.

CROP IN CHILLIE-THRIPS. Histologically the crop (Fig.7) is composed of the same layers as those of the oesophagus, but the chitinous intima (C. int.) is rather thicker. The epithelium (Epth.) is thrown into numerous, minute wavy folds, which stretch out during distension. The chitinous lining is developed into a number of ridges. The shape of epithelial cells is adapted to that of the chitinized ridges. The muscular coat is not generally well developed in this species. Of the two layers composing it the circular one (Circ.m.) seems however to be better formed than the longitudinal one (Long.m.).

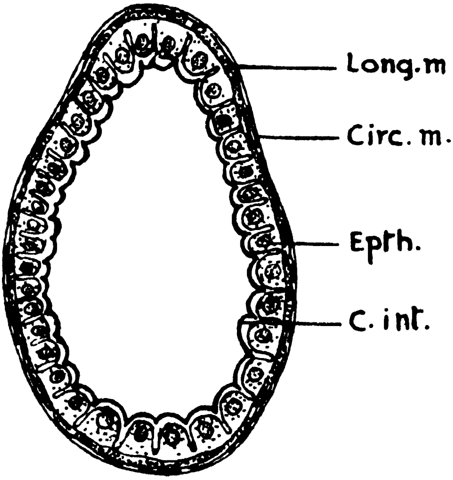

FIG. 7.

T. S. of the crop-like dilatation of the oesophagus of *S. dorsalis* (95 × 7)

C int. — Chitinous intima; Circ. m. — Circular muscles; Epth — Epithelium; Long.m — Longitudinal muscles.

THE OESOPHAGEAL VALVE. The oesophageal valve (Fig. 8) marks the termination of the fore-gut, and the mid-gut begins immediately behind it. It is a funnel-shaped structure formed by the projection of the posterior end of the fore-gut into the mid-gut. It is therefore double-walled, the inner and outer sides of which are formed of flat fore-gut epithelium lined with chitinous intima. The circular muscles (Circ.m.) situated between the inner and outer epithelia of the valve and forming more or less its core, function as strongly developed sphincters. At the junction of the oesophagus with the stomach are seen a few obliquely inserted muscle fibres (Ob. m.) outside the regular layer of circular muscle fibres.

The oesophageal valve, if the word implies a mechanism which automatically allows movement in one direction only, does not seem to function in this way in the insect under study, because the occlusion of the passage between the fore-gut and the mid-gut is effected apparently by the sphincter muscles. If the oesophageal valve were to have a valvular action, it should be closed by the pressure of the contents of the gut round the valve. But the oesophageal valve being a well developed double-walled structure strengthened by chitinous intima, such a pressure cannot be produced. Moreover, the mid-gut round the oesophageal valve is generally much weaker than the valve itself, and hence if the food exerts a pressure on the valve and the wall of the mid-gut, it is the latter that will bulge out rather than that the valve be closed.

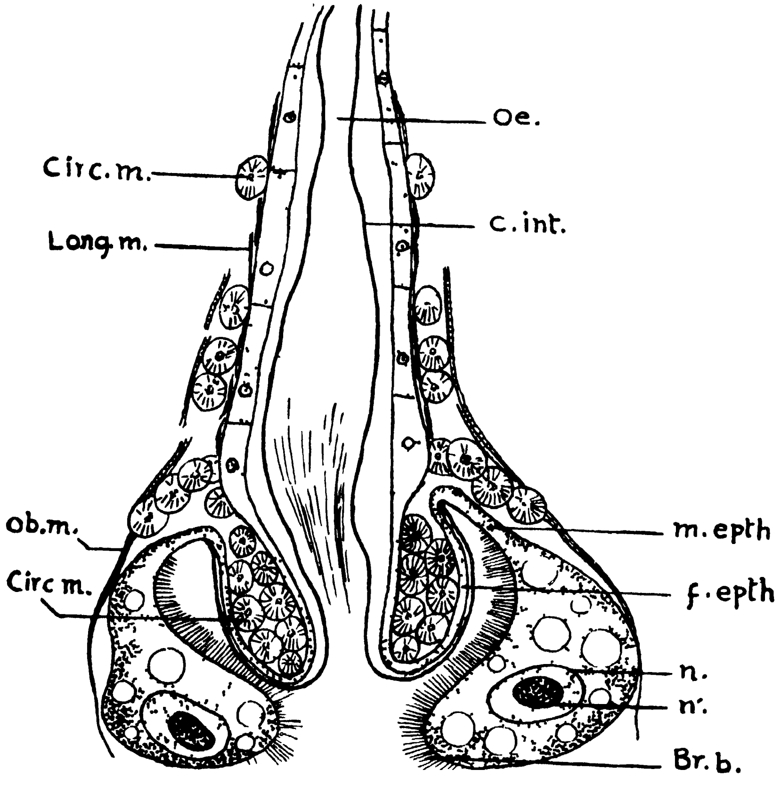

FIG. 8

L. S. of the oesophageal valve of *T. brunneicornis* (95×15).

Br. b —Brush-border; C. int.—Chitinous intima; Circ. m.—Circular muscles; f. epth.—Fore gut epithelium; Long. m.—Longitudinal muscles; m. epth.—Mid-gut epithelium; n.—Nucleus; n.—nucleolus; Ob. m.—Oblique muscles; Oe.—Oesophagus.

This consideration against the valvular action of the oesophageal valve suggests that the so called "oesophageal valve" of insects showed to be of such widespread occurrence never functions as a valve at all, but always as a sphincter between the fore-gut and mid-gut, and so Wiggleswoth (1930) suggests that the valvular projection of the fore-gut may have some other significance.

In Chillie-thrips the entrance into the stomach from the oesophagus is very narrow and is guarded laterally, by two chitinous plates (Fig. 9, C. pl)., supported by circular muscles (Circ. m.). Stretching across the chitinous plates are a few muscle strands (m. f.) which probably act as a strainer and allow the liquid food to pass through them on the relaxation of the circular muscles. This region is obviously comparable with the proventriculus of non-sucking insects. In other sucking insects as in Rose-thrips there is no trace of the proventriculus but they have the oesophageal valve instead. This structure in this particular case functions as the sphincter owing to the presence of circular muscles, which regulate the passage of food material from the oesophagus into the stomach.

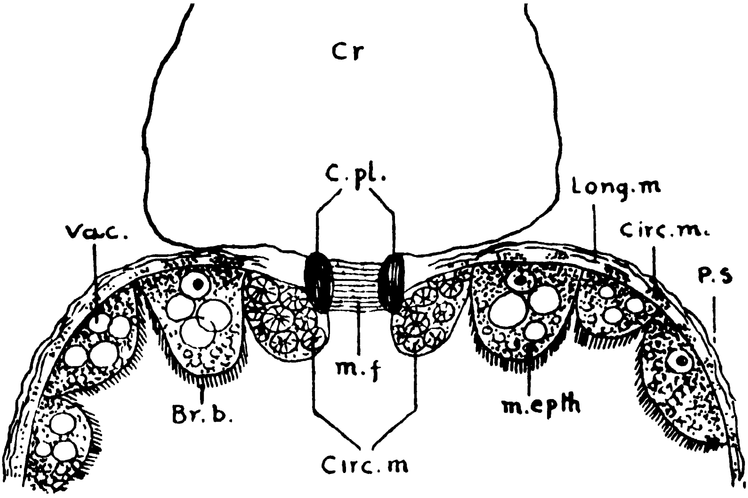

FIG. 9

L. S. passing through the junction of the fore-gut and the mid-gut of *S. dorsalis* showing the lateral chitinous plates guarding the entrance (95 × 10).

C. pl. – Chitinous plates ; Cr. – Crop ; Circ. m. – Circular muscles ; Long. m. – Longitudinal muscles ; m. epth. – Mid-gut epithelium ; n. – Nucleus ; p. s. – Peritoneal sheath ; Vac. – Vacuoles.

(B) MID-GUT:—The absence of the chitinous intima and the reversed position of the two layers of muscle fibres supply the histological key to distinguish the mid-gut from the fore-gut.

The mid-gut (Figs. 10 to 15) varies in its structure of epithelial cells lining the various regions. The different shapes and sizes of the cells in this region may be due to the difference in their secreting activities in various stages, and to their being compressed by the pressure exerted on by the excess amount of food juice sucked in.

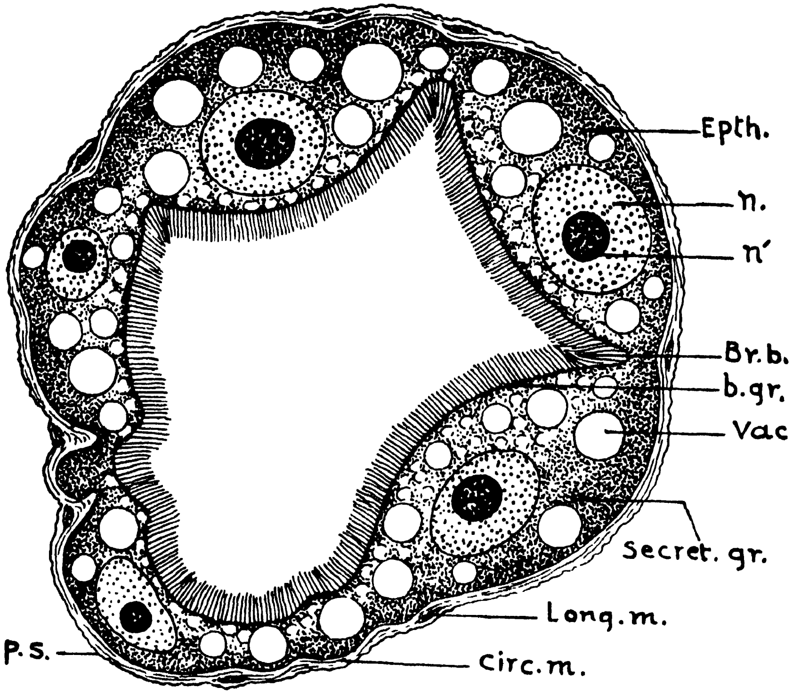

FIG. 10.

T. S. of the cylindrical stomach where the oesophagus projects. (95×15).

b. gr.—Basal granule: Br. b.—Brush-border; Circ. m—Circular muscles; Epth.—Epithelium; Long. m.—Longitudinal muscles; n.—Nucleus; n′.—Nucleolus; p. s.—Peritoneal sheath; Secret. gr.—Secretory granules; Vac.—Vacuoles.

CYLINDRICAL REGION—In Rose-thrips this part forming the proximal one-third of the looped mid-gut appears to be a seat of vigorous activity. The epithelial cells lining this part and as well as the rest of the mid-gut have a uniform structure and the changes observable in their appearance are simply due to the different phases of their secretory activities.

The epithelium (Epth.) in this region (Fig. 10) consists of tall columnar cells (22 μ to 24 μ in length and 20 μ wide) with rounded bases resting upon an indistinct layer of basement membrane closely merging into the underlying circular layer of muscles. Each cell has an ovoid nucleus (n.) (10 μ across) in the centre, with a large round nucleolus (n') situated towards the free end. In the resting stage the columnar cells are fairly regular in shape, but assume various forms during their secretory activity. The cytoplasm appears to be granular (Secret. gr.), and in it are seen a number of clear conspicuous rounded vacuoles (Vac.) which largely change their form in the wake of physiological activity.

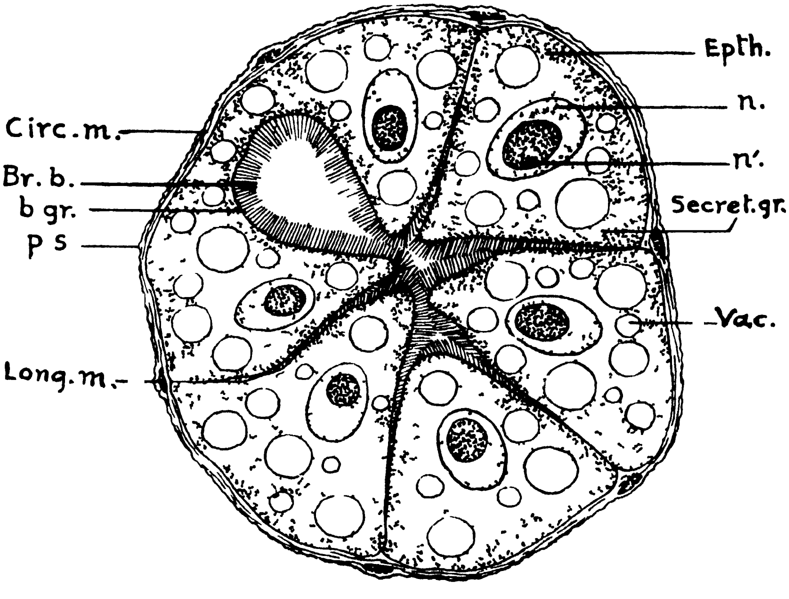

FIG. 11.

T. S. through the anterior half of the cylindrical portion of the mid-gut of *T. brunneicornis* (95 × 15).

b. gr.—Basal granule ; Br. b —Brush-border : Circ. m.—Circular muscles ; Epth.—Epithelium ; Long. m —Longitudinal muscles ; n.—Nucleus : n'.—Nucleolus ; p. s.—Peritoneal sheath ; Secret. gr.—Secretory granules ; Vac.—Vacuoles.

BRUSH-BORDER. In the resting stage there arises from the free edge of the cell a brush-border or a fringe (Br. b.) aptly described as such in the intestine of the Migratory Locust by Nenyukov and Parfentjev (1929). It is composed of numerous fine protoplasmic filaments which appear to be in direct continuity with the protoplasm of the cell. The filaments are remarkably cilia-like in appearance. They are free from and independent of one another throughout their whole length, with no trace of transverse connectives or of any trace of peripheral membrane joining them. These filaments project quite regularly from the free surface of the cell except at the place where they are disturbed by the secretion-droplets coming out from the cells. At the base of each filament is seen a black spot which is considered to be the basal granule (b. gr.) or a part of the centrosome. These fine filaments cannot be considered as cilia on account of their being devoid of immovable basal rods and the distal and basal granules, which are so characteristic of cilia in general. Likewise the free border of these cells cannot be considered as "striated-border", since the processes are very long and are in no way held together by a cement-substance. It would appear then that these brush-border elements are simple, filamentous outgrowths from the upper surface of the cell and are never capable of autonomous movement. In the resting stage the brush-border of the cells shows a definite arrangement, but in the secreting stage the free margin is often jagged and irregular.

SECRETION. Discrete droplets of secretory fluid in the form of vesicles are seen extruded into the lumen (Fig. 12). Such a type of secretion has been described as a special type of merocrine-vesicular secretion (Buchmann, 1928). Such vesicles are stated to be artificial by Pavlovsky and Zarin (1922), while Henson (1929) working on the larvæ of *Vanessa* claims that these so-called merocrine secretions are the result of the process of cellular degeneration.

The filamentous brush-border is not seen to extend over the enlarging secretion vesicles (Secret. ves.) before or after they are constricted and pinched off from the free edge of the cell. The cells of the gut often contain conspicuous vacuoles and their presence usually indicates the absorptive as well as the secretory condition of the gut.

The formation and development of the vacuoles is difficult to demonstrate, but it is interesting to note that vacuoles may be observed near the nucleus and towards the distal end of the cell. In the opinion of Woodruff (1933) these globules, so often observed by earlier investigators in insects, are due to technical mistakes. He further adds that they are never seen in specimens fixed in Bouin, Fleming, and Kleinenberg, though easily found in material treated with " formol-acetic alcoho ".

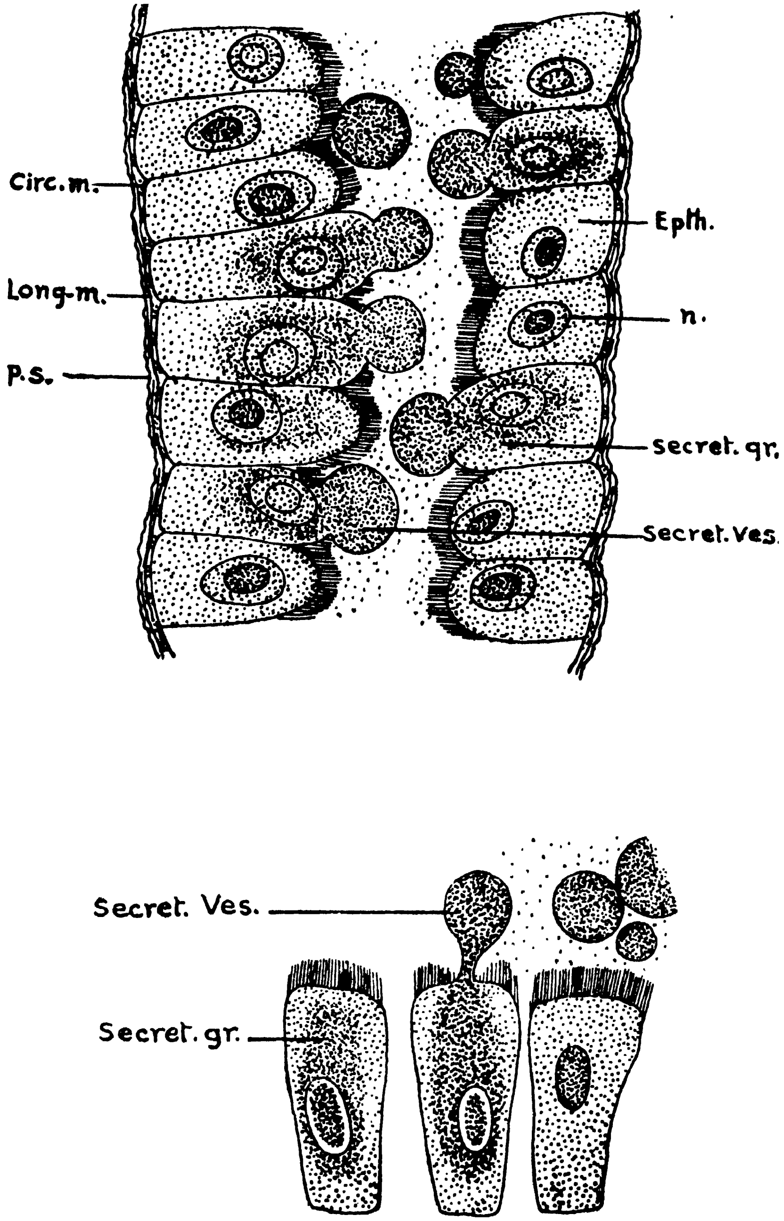

FIG. 12

L. S. through the cylindrical portion of the mid-gut showing the secretory phases (95 × 10).

Circ. m. — Circular muscles ; Epth. — Epithelium ; Long. m. — Longitudinal muscles ; n. — Nucleus ; p. s. — Peritoneal sheath ; Secret. gr. — Secretory granules ; Secret. ves. — Secretory vesicles.

DISTAL LOOP IN ROSE-THRIPS. The histological characteristic of the *ascending* and *descending* limbs of this loop (Fig. 13) lies in the complete change in the structure of the epithelium. The tall columnar cells of the stomach here give place to short, flat cells lengthened in the tangential direction. The cytoplasm contains relatively more vacuoles (Vac.) than in the preceding region, the only likeness being the presence of the brush-border (Br. b.) at the free end of the cell. The lumen of this part of the mid-gut is gorged with food material (F.).

The histological characters of the epithelium of the stomach and of the distal loop indicate that copious secretion is poured on the food in the former and digestion is completed in the latter where the secretion has time to act on it. The vacuoles seen in the cells of the distal loop may have arisen, therefore, in the course of food absorption. Further the lumen of the stomach is usually filled with secretory vesicles and portions of secretory cells, while the lumen of the distal loop generally contains a

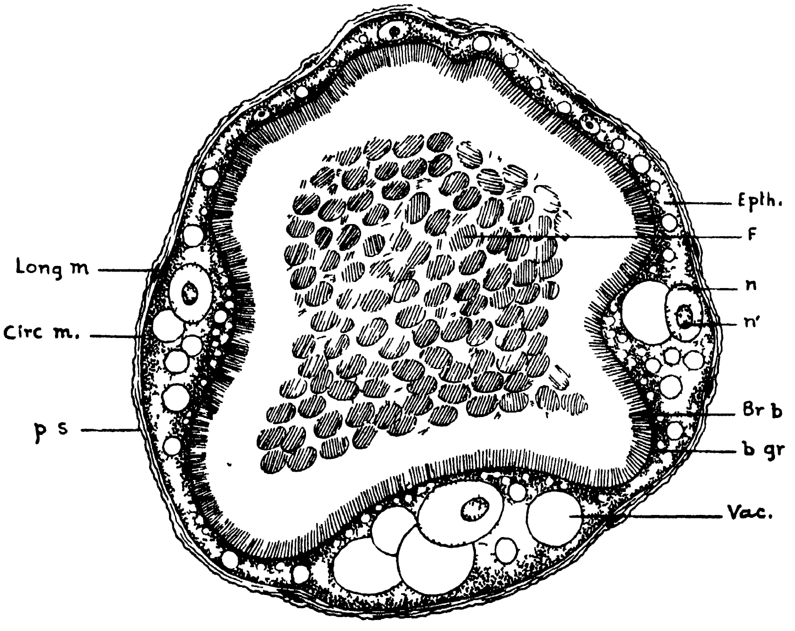

FIG. 13.

T. S. of the ascending limb of the mid-gut (×950)

b. gr.—basal granule; Br. b.—Brush-border; Circ. m.—Circular muscles; Epth—Epithelium; F.—Food material· Long. m.—Longitudinal muscles; n.—Nucleus; n'.—Nucleolus; p. s.—Peritoneal sheath; Vac.—Vacuoles.

food-cylinder. It may, therefore, be presumed that the distal loop of the mid-gut functions as the main absorptive chamber.

MUSCULATURE. The muscles of the mid-gut consist of internal circular and external longitudinal fibres. Out of these two layers the circular muscles (Circ. m.) constitute the main layer. The layer of longitudinal muscle fibres (Long. m.) is formed of bundles or bands, six to eight in number and spaced widely. A peritoneal layer (p. s.) consists of a fine, loose, wavy band covering the muscularies.

MID-GUT IN CHILLIE-THRIPS. The epithelial cells of the mid-gut as described in the Rose-thrips appear to be rather different in shape, both in the anterior and the posterior regions. The cells (Epth.) in the anterior region (Fig. 14) are more or less cuboidal with the nucleus (n) situated at the base. The cytoplasm

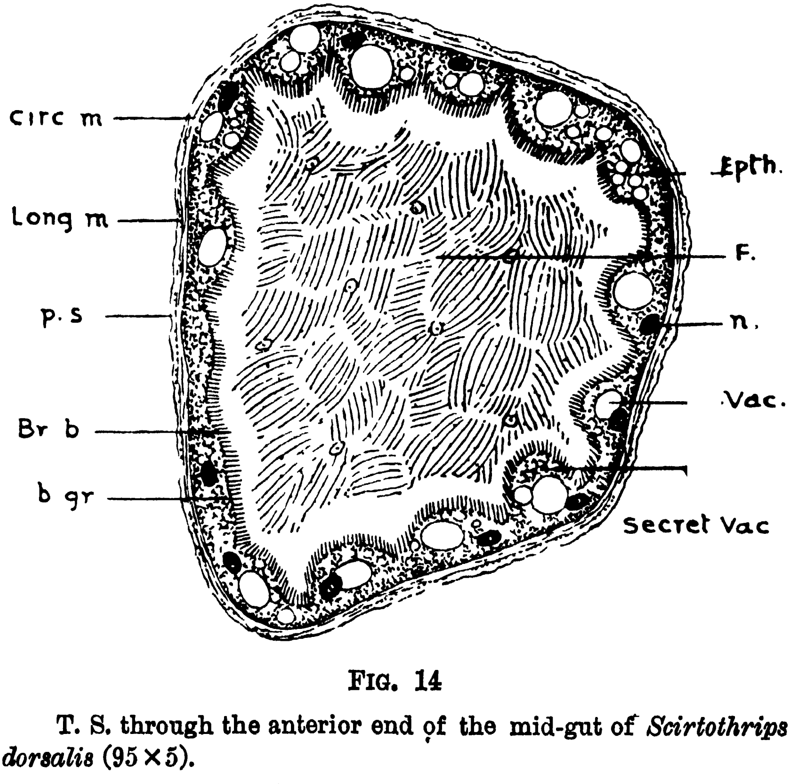

FIG. 14

T. S. through the anterior end of the mid-gut of *Scirtothrips dorsalis* (95 × 5).

b. gr.—Basal granule; Br. b.—Brush-border; Circ.m.—Circular muscles; Epth.—Epithelium; F. Food-material; Long. m—Longitudinal muscles; n—Nucleus; p. s.—Peritoneal sheath; secret. vac.— Secretory vacuoles; Vac—vacuoles;

of these cells is full of large vacuoles (Vac.) pushing the nucleus to one side. These large conspicuous vacuoles give a spongy appearance to the cytoplasm. The cells (Epth.) of the posterior region of the stomach (Fig. 15) of a well-fed insect show that they are distinctly flattened, due either to the elimination of the secretory products or to the pressure exercised by the excess of juice sucked in by the insect. In this region the food forms a solid cylindrical core (F.) in the centre of the lumen, almost touching the epithelial cells and suggesting the coagulated juice being enclosed in a peritrophic membrane. But a careful examination of the sections at different regions, particularly those at the anterior end, reveals that the semblance of a solidified juice being surrounded by a peritrophic membrane was mainly due to the instantaneous coagulation of the juice while fixing the insects. The free ends of the cells are lined by a brush-border (br. b.) the protoplasmic processes of which are almost half the length of those in the Rose-thrips.

The method of secretion here also is of the same merocrine-vesicular type.

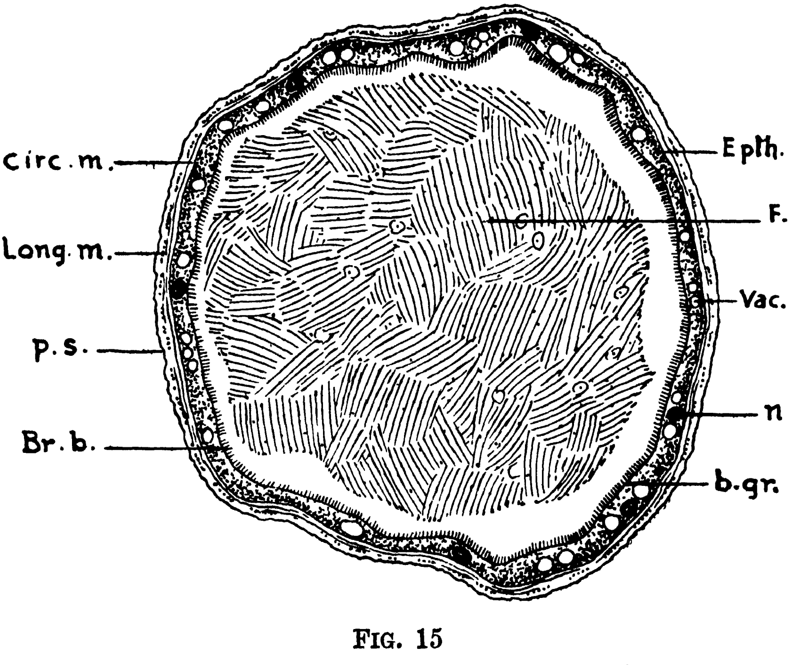

FIG. 15

T. S. through the posterior end of the mid-gut (95 × 5).

b. gr.—Basal granule; Br. b.—Brush-border; Circ. m.—Circular muscles; Epth.—Epithelium; F.—Food-material; Long. m.—Longitudinal muscles; n.—Nucleus; p. s. Peritoneal sheath; Vac.—Vacuoles.

The basement membrane completely merges into the underlying muscular layer and hence cannot be clearly marked as a separate layer.

MUSCULATURE :—Compared with the musculature of the Rose-thrips, both the layers of the muscle fibres are poorly developed and the longitudinal muscles (Long. m.) are not arranged in groups or bundles but form a thin layer. The peritoneal layer (p. s.) as in the Rose species, is seen as a separate wavy band investing the muscularies.

(C) HIND-GUT. Histologically, this region could be distinguished from the mid-gut by the reappearance of the chitinous intima which is characteristic of the fore-gut. The cells of the epithelium show little evidence of having any secretory function. The muscularies show better development than in any part of the previous two regions.

Although the hind-gut has been externally divided into the anterior ileum and the posterior rectum there are no marked histological differences between the two.

HIND-GUT IN ROSE-THRIPS :—The epithelial lining of the hind-gut (Figs. 16, 17) is made up of small, flattened, non-glandular cells (Epth.) with a nucleus (n) in the centre of each cell. The intima (C. int.) is fairly thick and chitinous.

The rectal valve (Figs. 16, 17. Rect. V.) shows no marked variations in its epithelial lining and the intima, but in the fold of the valve are seen well developed circular muscles (Circ. m.) which function as sphincters. At the posterior end of the ileum stretching across its lumen and situated a little above the rectal valve, are seen a few muscle strands (m.f.) similar to those found at the entrance of the mid-gut in the Chillie-thrips.

The epithelial lining of the rectal sac does not show any folds but it is put into 3 or 4 folds in the terminal part of the rectum proper as in the oesophagus. The chitinous intima (C. int.) in the latter is thicker than that of any other portion of the hind-gut.

MUSCULATURE. The muscularis includes the internal circular (Circ. m.) and external longitudinal fibres (Long. m.), which are arranged as in the region of the mid-gut. Additional bands of circular muscles are also found to be present outside the longitudinal layer. The circular muscles at the end of the rectum are well developed and form a sphincter. On the whole the musculature of this region appears to be much thicker than that of any of the preceding parts of the gut.

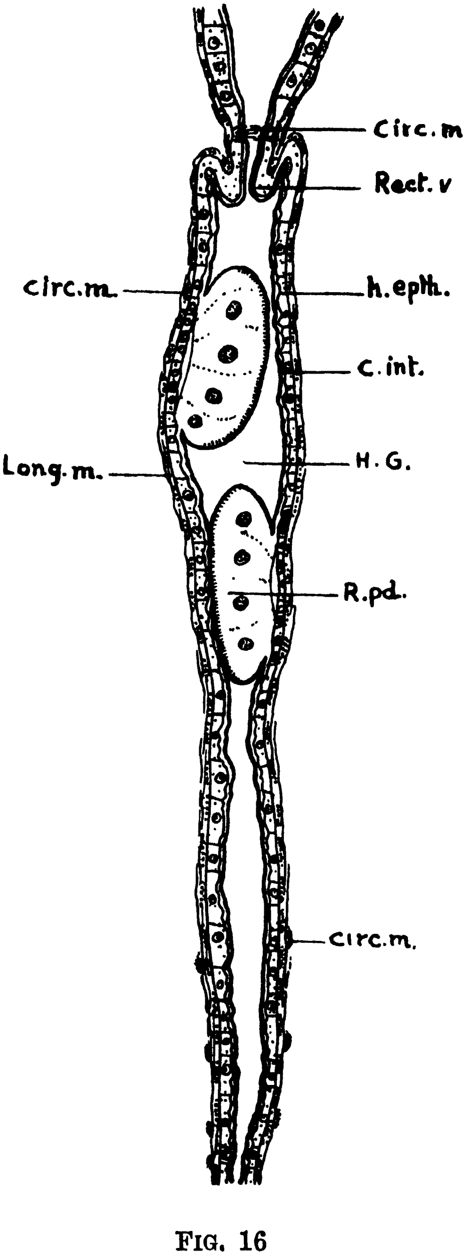

FIG. 16

L. S. of the hind-gut of *T. brunneicornis* showing the rectal valve, the rectal pads and the anal opening (40 × 10).

C. int. – Chitinous intima ; Circ. m. – Circular muscles ; H. G. – Hind-gut ; h. epth. – Hind-gut epithelium ; Long. m. – Longitudinal muscles ; R. pd. – Rectal pad ; Rect. V. – Rectal valve.

HIND-GUT IN CHILLIE-THRIPS. As in the Rose species, the epithelium of the hind-gut in the case of Chillie-thrips is made up of non-glandular cells, but their cell boundaries are not clearly defined. The cells are comparatively short and flattened with the nucleus situated at the centre of each. The free ends of these cells, as in the Rose species, are lined with the chitinous intima. In no part of the hind-gut the epithelium forms a wavy line or is thrown into conspicuous folds. The rectal valve in this species is similar in structure to that of Rose-thrips.

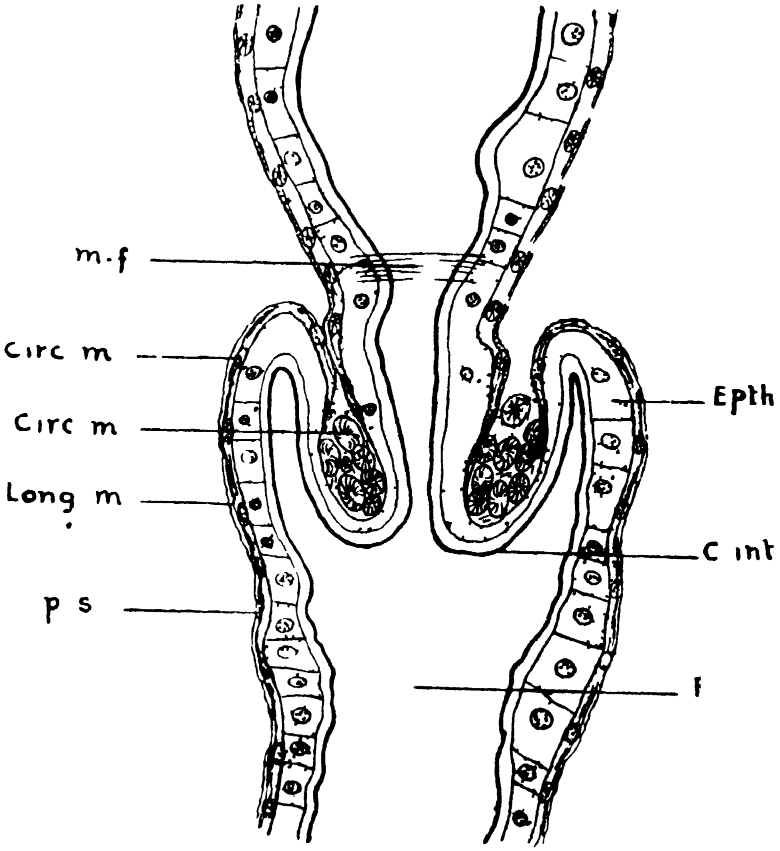

FIG. 17

L. S. of the rectal valve of *T. brunneicornis* (95 × 15).

C. inst. — Chitinous intima ; Circ. m. — Circular muscles ; Epth. — Epithelium ; Long. m. — Longitudinal muscles ; m. f. — Muscle fibres. p. s. — Peritoneal sheath. R. — Rectum.

The musculature of this region when compared with that of Rose species appears to be poorly developed. The longitudinal muscles form an outer homogeneous layer and are not grouped into bands which are so conspicuously seen in the mid- and the hind-gut of Rose-thrips. The additional outermost circular layer of muscles of Rose-thrips seems to be altogether absent in this species. The innermost circular layer of muscles is well developed only at the terminal portion of the rectum where it forms a sphincter.

RECTAL PADS. There are two pairs of rectal pads (Fig. 16. R. pd.) in the Rose-thrips situated one behind the other, on the right and left sides of the rectal sac (R. sc.). Each of them (65 μ by 24 μ) is a hollow, small, oval, pad-like thickening of the rectal wall with its long axis parallel to the rectum.

Histologically the rectal pad (Fig. 18) is found to be in the form of a small sac whose inner wall is made up of high columnar

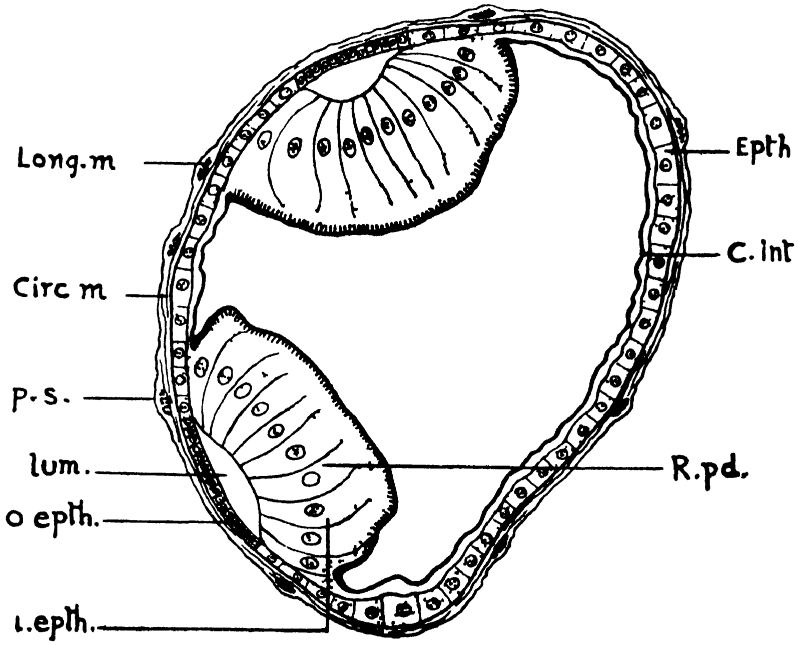

FIG. 18

T. S. of the dilated rectum of *T. brunneicornis* showing the rectal pads (95 × 10).

C. int. – Chitinous intima ; Circ. m. – Circular muscles ; Epth – Epithelium ; i. epth. – Inner epithelium ; Long. m. – Longitudinal muscles ; lum. – Lumen ; o. epith – Outer epithelium ; p s. – Peritoneal sheath ; R. pd. – Rectal pad.

epithelial cells with large nuclei (n) and 12 μ across at the centre. The outer wall is formed of small flattened cells just like those of the surrounding epithelium. A very small lumen is present between the two cell-layers. It is owing to the presence of this lumen that the pad is considered as hollow. Such pads are present in Neuroptera and certain Hymenoptera (Tonkov, 1923, 1925). The intima (c. int.) is usually thin over the surface of each pad but forms a thickened rim around its margin.

The inner wall (i. epth) according to Evenius (1933) is made up of the normal epithelial cells of the rectum, while the outer wall (o. epth.) is supposed to be derived from the cells lying originally in the body-cavity around the hind-gut, which gradually approach the rectum and become stratified upon it to form the outer wall of the rectal pads.

In structure, position, and arrangement the 4 rectal pads (Fig. 19) in the Chillie-thrips exactly resemble those in Rose-thrips, but differ only in their being more rounded.

FUNCTION OF RECTAL PADS. With regard to the function of the rectal pads nothing definite can be stated, and various functions have been attributed to them by several workers. It is supposed by some workers that these pads are of glandular nature and they have divided the proctodæum into pre-glandular, glandular, and post-glandular regions as mentioned before.

The question that these pads serve to break up the peritrophic membrane does not arise here, since the latter seems to be altogether absent in the species under study. Some workers suggest that they aid in the elimination of carbon-dioxide from the blood and absorb food residue from the rectum.

Recently Wigglesworth (1932) has advanced the theory that these organs and the rectal epithelium of insects reabsorb water from the excrement before it is discharged, and thus play a very important role in the conservation of water-content in the insect body. But the chitinous intima lining the inner surface of the rectal epithelium and the thick and denser intima covering the rectal pads do not appear to particularly adapt these organs to serve any of the above roles attributed to them.

(D) SALIVARY GLANDS. In *Taeniothrips Brunneicornis* there are two pairs of salivary glands of unequal lengths (Fig. 1), the shorter (B_2) being inner, the longer (B_1) outer. The shorter pair (133 μ by 44 μ) extends from the anterior end of the meso-thorax to the middle third of the meta-thorax. The longer pair (183 μ by 55 μ) begins at the same level and extends posteriorly upto the first abdominal segment.

Both the glands are elongated, ribbon-shaped, hollow sacs with rounded posterior ends. Each is superficially divided into a number of pseudo-segments by small transverse grooves which number from 4 to 6 in the case of the shorter and 8 to 10 in the longer one. A very fine lumen extends along the centre of the gland.

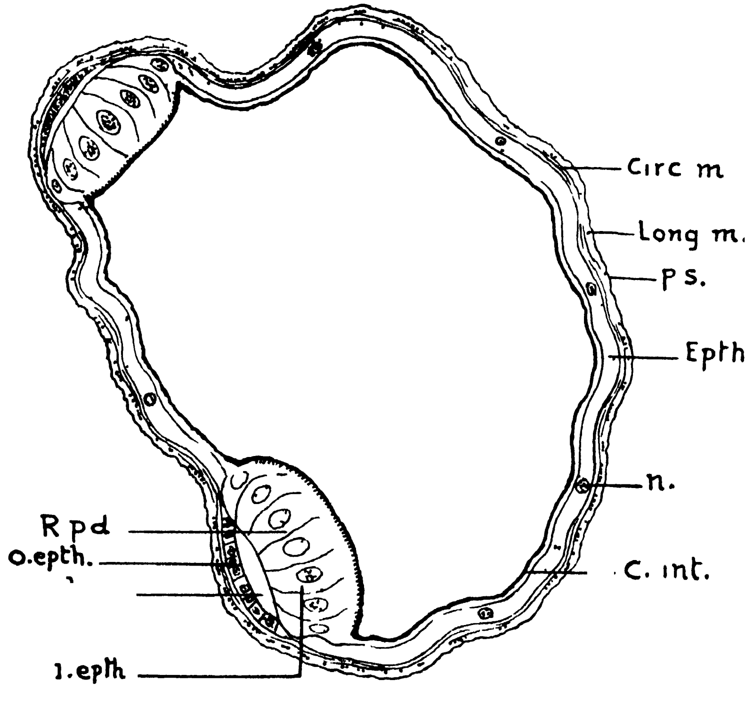

FIG. 19.

T. S. of the dilated rectum of *S. dorsalis* showing the rectal pads (95 × 7).

C. int. — Chitinous intima; Circ. m — Circular muscles, Epth — Epithelium; i. epth — Inner epithelium; Long. m — Longitudinal muscles, lum. — Lumen, n — Nucleus, o. epth. — Outer epithelium; p s. Peritoneal sheath; R. pd. — Rectal pad.

The ducts of the shorter glands are of a uniform diameter throughout, and continue their course anteriorly, dorso-lateral to the oesophagus, as separate and distinct tubes. On entering the head region they unite to form a common duct which runs along with the common duct of the longer pair.

The ducts of the longer pair also run dorso-lateral to the oesophagus and extend anteriorly upto the beginning of the pro-thorax as slender tubes. In the head region, however, they widen out to form reservoirs (Fig. 1. C) which extend upto the circum-oesophageal nerve ring where they unite to form a common duct. Both the common ducts run forward dorso-laterally to the oesophagus till they abruptly bend downwards and run to the base of the "Y" shaped chitinous piece. They join at this place to form a median common duct which runs through the median groove of the stem of the above piece, and opens to the outside between the distal ventral ends of the maxillary stylets. The salivary secretion is thus poured into the punctures made in the host-plant by the mouth parts.

The median common salivary duct does not open anteriorly into the oesophagus, although mentioned by Sharga (1933) in *Aptinothrips rufus.* Our observations agree with those of Peterson (1915) in *Heliothrips femoralis,* in that that the median common duct continues into the median limb of the "Y" shaped chitinous piece upto the apex of the mouth-cone which opens to the outside.

The "Y" shaped chitinous piece (Fig. 2, B) which is located posterior to the pharynx is a characteristic structure found in all thrips. Distinct muscle bands are attached to the tips of the arms of the "Y" at one end and to the postero-dorsal part of the pharynx at the other. These muscles control the flow of secretion from the salivary ducts into the median common duct and also its flow to the outside.

The wall of a salivary duct is comparatively thin and encloses a fine lumen. The cell boundaries of the epithelial lining are not clearly defined and several nuclei are seen at intervals. The peritoneal sheath of the glands is continued to form an outer covering of the ducts. The chitinous ring-like thickening of the salivary ducts of other insects is not seen here.

HISTOLOGY OF SALIVARY GLANDS. Each lobule of the gland (Fig. 1. B_1, B_2) is made up of a large cuboid cell which is seen to be filled with granular protoplasm. The ovoid nucleus (n) (10 μ across) has also a granular appearance and is found at the basal end of the cell. In the centre of the nucleus there is a large, rounded, deeply-stained nucleolus. The secretory activity appears to be confined to almost all the lobules except the anterior one.

The beginning of the secreting activity of the cell (Fig. 20) is indicated by the appearance of a number of small, rounded alveoli

(B. Alv,) at the base of the cell, which thus give an alveo-granular appearance to the protoplasm (D), which is therefore stained unevenly. These alveoli become larger and increase in number with the result that they completely fill up the cell forming a delicate network in the cytoplasm (E). All the alveoli towards the inner end of the cell are coalesced to form a large single vacuole, occupying the major portion of the cell, with the result that the granular cytoplasm (Secret. gr.) appears to be pushed towards the periphery of the cell (F).

The morphological and histological details of the salivary glands in Chillie-thrips are essentially the same as those of Rose species.

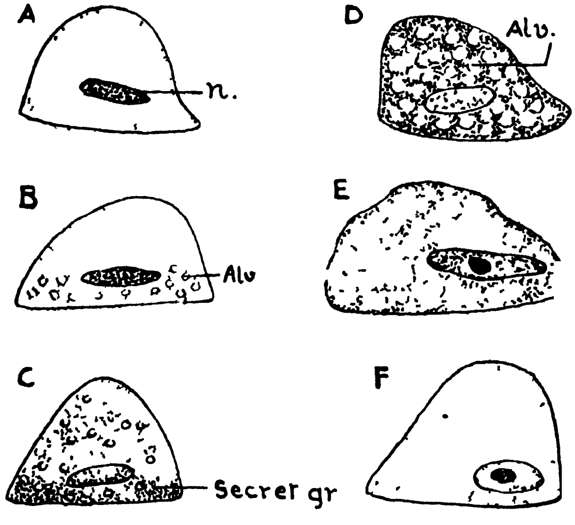

FIG. 20.

Schematic links of the secretory phases of the cells from the salivary glands in *T. brunneicornis*.

Alv.—Alveoli; n.—Nucleus; Secret. gr.—Secretory granules.

(E) THE MALPIGHIAN TUBES. There are four slender, moderately long (621 μ in length), cylindrical malpighian tubes two of them being directed anteriorly and the other two posteriorly (Fig. 1A. Mt.). The anterior pair (430 μ) is the longer of the two and extends upto the second abdominal segment. The posterior pair measures about one-third the length of the anterior one and reaches as far as the end of the rectal sac. The posterior tubes are more or less applied to the sides of the hindgut and the anterior ones appear to lie free in the body cavity.

The tubes open at the junction of the mid-gut and the hind-gut through a common canal passing through the median bridge formed by the two malpighian tubes of each side (Fig. 21) and appear somewhat "H" shaped in form. The lumens of the anterior and posterior tubes of each side continue separately in the transverse bridge till they open in the region of the ileum through a common aperture. This method of opening through a common canal was first observed and described by Uzel (1895) in *A fasciatus.* The tubes taper towards their free ends measuring 11 μ wide at the apex, 16 μ wide in the middle and 20 μ wide at the base. In fresh dissections the malpighian tubes appear brownish in colour and finely granular in contents.

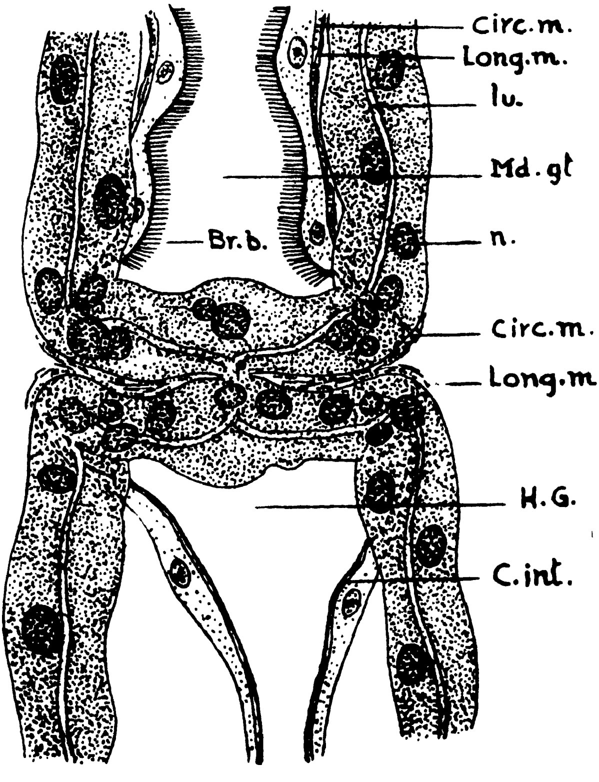

FIG. 21

Horizontal section through the intestine showing the origin of the malpighian tubes in *T. brunneicornis* (95 × 10).

Br. b. – Brush-border ; Circ. m. – Circular muscles ; C. int. – Chitinous intima ; H. G. – Hind-gut ; Long. m. – Longitudinal muscles : lu. – Lumen of the tube ; Md. gt. – Mid-gut ; n. – Nucleus.

HISTOLOGY OF THE MALPIGHIAN TUBE. A transverse section of the tube (Fig. 22) at any region shows that it is made up of 3 to 6 large cuboidal epithelial cells (Epth) which vary in size and shape according to their physiological condition. At some places the epithelial cells project far into the lumen (lum.) of the tube and thus almost occlude the passage. The nuclei (n) are large (8 μ to 12 μ across) and stain deeply. The free ends of the cells are lined with a brush-border similar to that of the mid-gut. A similar thick coating of fine cilia-like processes projecting from the inner ends of the cells, is observed by Noel and Tahir (1929) to be present in the tubes of *Bombyx mori*, almost filling up the lumen. The elements of the brush-border of the malpighian tubes in insects according to Shiwago (1915) are chondrioconts (mitochondria) which are found near the base of the cell and which migrate finally to be shed into the lumen of the tube where they occur in the form of excretory granules. Striated or ciliated appearance at the free margin of each cell bordering the cavity of the tube is, in the opinion of Imms (1935), due to the presence of pore-canals.

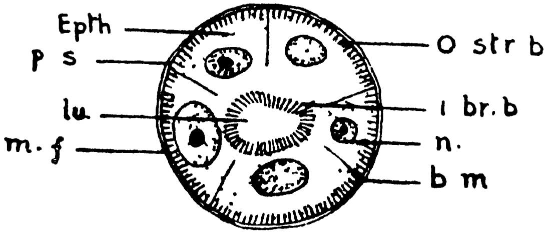

FIG. 22

T. S. of a malpighian tube (95 × 15).

b. m. — Basement membrane ; Epth. — Epithelium ; i. br. b. — Inner Brush-border . lu. — Lumen ; mf. — Muscle fibre ; o. str. b. — Outer striated border ; n. — Nucleus ; p. s. — Peritoneal sheath.

Towards their outer margin also the cytoplasm of the cells shows very fine striations (o. str. b.) at right angles to the basement membrane forming an outer striated zone already observed by Veneziani (1925).

The entire epithelium rests on a basement membrane (b. m.) which itself is invested by a thin peritoneal sheath (p. s.). In the latter are seen scattered a few muscle fibres (m. f.) which do not form a definite layer. The junction of the malpighian tubes with the gut (Fig. 22) is lined by a few longitudinal (Long. m.) and circular muscle fibres (Circ. m.) which are continuous with the musculature of the intestine. Similar continuations of the musculature of the intestine on the wall of the malpighian tube have been observed by Eastham (1925) in *Drosophila* and *Calliphora*, and by Wigglesworth (1931 b) in the ampullae and the lower ends of the malpighian tube of *Rhodinus*.

Although the malpighian tubes are the outgrowths of the proctodaeum, histologically they resemble the mid-gut, in as much as the free ends of the cells are not lined by chitinous intima. Henson (1932) not only has shown the endodermal origin of the malpighian tubes but he further believes that in all Lepidoptera the functional parts of the tubes are of endodermal derivation and that only the terminal ducts opening into the hind-gut are of proctodaeal origin.

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OVARIAN TUMOURS

A STATISTICAL AND CLINICAL STUDY

By

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The present paper is based on a review of a series of ovarian neoplasms that were consecutively treated in the Gynæcological department of the K. E. M. Hospital, Bombay, by my colleagues and myself. The history of every case was carefully taken and every specimen which was removed at the operation was histologically examined by the Pathology Department of the Hospital.

The special object of the study was to determine the age incidence and the incidence of malignancy of ovarian Tumours in Bombay.

The tumours removed varied in size. The smallest being the size of a duck's egg and the largest with an abdominal girth of 42 inches. (Fig. 7).

I have excluded from this series, Broad Ligament cysts and Follicular cysts, because they are purely distention cysts and not neoplasms.

I have attempted to group the tumours according to Meyers-Pfannestiel scheme, *viz.*

A. Epithelial tumours.		
1. Innocent.		
(a) Cystoma simplex. ...	... 48	38.09 %
(b) Cystadenoma Pseudomucinosum	... 34	38.98 „
(c) Cystadenoma serosum Papillare	... 3	2.38 „
2. Malignant-Primary.		
(a) Carcinoma adenomatosum	... 12	9.28 „
(b) Carcinoma Solidum	... 10	7.93 „
(c) Carcinoma Papillomatosum	... 5	3.96 „
(d) Cystadenoma pseudomucinosum with secondary malignant changes	... 2	1.58 „
B. Connective tissue tumours.		
1. Innocent.		
Fibroma	... 3	2.38 „
2. Malignant.	nil.	

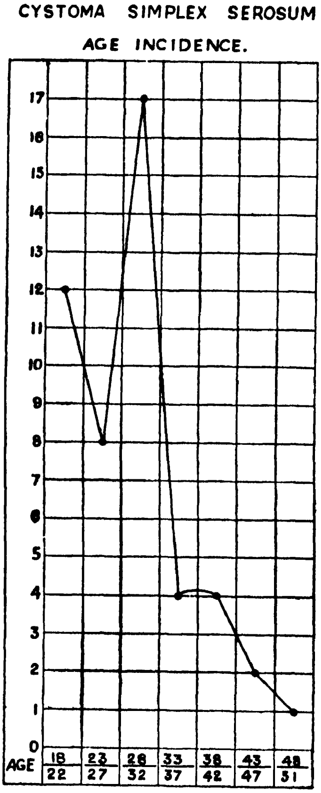
C. Mixed tumours and teratomata.		
1. Innocent.		
Dermoid cysts	... 4	3.15 „
2. Malignant.	nil.	
D. Fimbrial cysts	... 4	3.15 „
E. Chocolate cysts	... 1	.79 „
Total	... 126	100.00

CYSTOMA SIMPLEX SEROSUM

These neoplasms constituted the largest number of tumours in my series *i.e.*, 48. The largest tumour was the size of a full term pregnant uterus and the smallest the size of a duck's egg.

Age incidence was as follows:—

The youngest patient was 18 years of age and the oldest 49. Graph 1 illustrates the incidence.



Graph 1.

Menstrual and Obstetric Histories. Between the ages of 18 and 45, menstruation was regular in six patients and scanty in 22. Three complained of dysmenorrhœa, one of epimenorrhagia, one of menorrhagia, two of amenorrhœa and two of lactational amenorrhœa. Between the ages of 45 and 51 there was menopause.

Three patients were unmarried and one was a child widow. 22 bore children (1 to 7). The two with lactational amenorrhœa developed the neoplasm during the puerperium. In both of these cases the duration was of two months and the tumours were the size of 7 and 8 months pregnant uterus, respectively.

Symptoms and complications. Four patients complained of acute abdominal pain and tenderness. In these the pedicle of the tumor was twisted. Three others complained of acute abdominal pain, temperature and difficulty in micturition ; in these the tumours had suppurated. In one of these the tumour had burst in the pelvis. One complained of colicky pain in the abdomen ; in this case the tumour was an abdominal parasite and was adherent to the omentum and the intestines. It was the size of a pomelo. Nine patients complained of abdominal swelling, discomfort and a dull abdominal ache. In these the tumours were large and varied in sizes, from 7 months to full term pregnant uterus. Four patients gave histories of puerperal infection, subsequent sterility and hypomenorrhœa. In these the tumours were adherent to the posterior layer of the Broad Ligament and to the pelvic floor. (pseudo broad ligament cysts). The appendages on the opposite side showed signs of chronic inflammation. One patient complained of menorrhagia. In this case the uterus was the size of a bull's heart, due to multiple fibroids. In five patients the tumours were bilateral.

Treatment. Salpingo-oophorectomy was performed in all cases except in one in which the cyst had suppurated and burst. The complete removal of the cyst wall was not possible. Salpingo-oophorectomy with hysterectomy had to be performed in four cases, *viz.*, in the three adherent (pseudo broad ligament) cysts and in the case of Fibroid of the uterus.

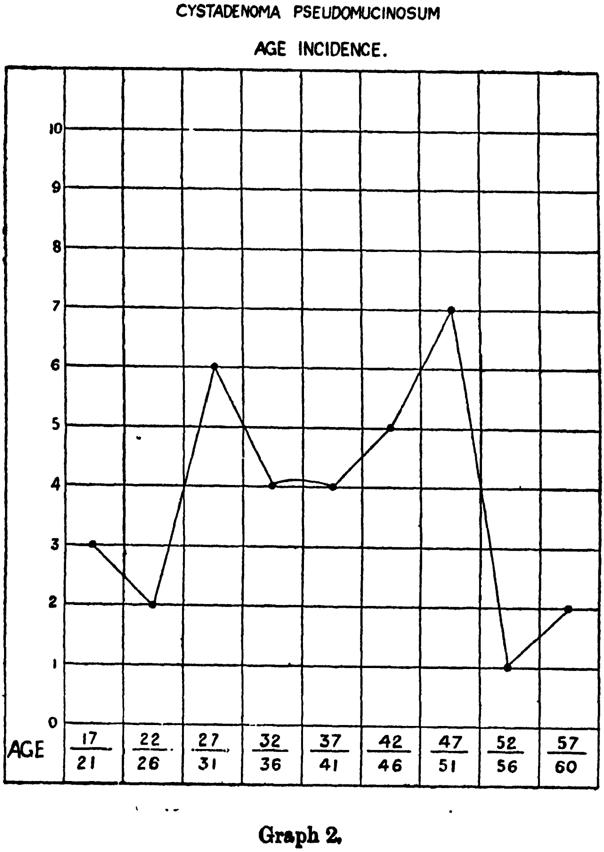
Operative Mortality. Two patients died. The one with the parasitic cyst died of intestinal perforation on the third day. She had suffered from typhoid fever 6 months before admission to the Hospital. Post-mortem revealed scars of old healed intestinal ulcers. Two of these were torn, probably due to the manupulations during the operation. One died of post operative pneumonia on the sixth day of the operation.

CYSTADENOMA PSEUDOMUCINOSUM.

There were 34 cases of cystadenoma Pseudomucinosum in my series. The smallest tumour was the size of a bull's heart and in the largest the girth measurement of the patient was 42 inches. (Fig. 7). The average size was that of a six months pregnant uterus.

With the advance of gynæcological surgery in Bombay, to-day, patients seek admission to the public hospitals earlier than they did in olden days, with the result that it is rare now to see a mammoth ovarian tumour. I remember having operated on a mammoth ovarian, 17 years ago, when I was associate Professor of Midwifery and Gynæcology at the Grant Medical College and Hon. Obstetrician to Sir J. J. Hospital. The tumour weighed 217 Lbs.

Age incidence. The youngest patient was 17 years of age and the oldest 50. The incidence was greater between the ages of 27 and 51. Graph 2 illustrates the age incidence.



Graph 2.

Menstrual and Obstetric Histories:—One patient was unmarried and two were child-widows. Between the ages of 17 and 40, menstruation was normal in seven cases, scanty in five, one patient complained of menorrhagia and two, each aged 18, of amenorrhœa, for two years. Between the ages of 40 and 60 menopause had set in at different periods. Twenty seven bore children (from 1 to 11) and four were sterile. One patient was confined 13 months before admission to the Hospital.

Symptoms and complications:—Twenty patients complained of abdominal swelling and discomfort. Four complained of epigastric pain and vomitting after food, five complained of urinary disturbances; two of these had retention of urine, due to impaction of the tumour in the pelvis. One suffered from pyelitis. Two presented the syndrome of an acute abdomen. In these the pedicle of the tumours was found twisted.

Genital hernia was met with in two cases, submucous Fibroids in one and endometriosis uteri in one other.

Five tumours were badly adherent to the abdominal wall, omentum, intestines and to the pelvic floor. Inflammatory leisions on the opposite side were found in 6 cases. In two other there were large Hydrosalpinges.

Treatment:—Salpingo-oophorectomy was performed in all cases. Whenever the ovary and the tube were found diseased on the opposite side, they were removed. Hysterectomy was performed twice once for fibromyoma uteri and at other time for endometriosis.

Operative Mortality:—Out of 34 patients operated upon three died, one of pneumonia, one of post-operative shock and the third of pyelitis.

CYSTADENOMA SEROSUM PAPILLARE

There were only three tumours belonging to this group in my series. A very low incidence indeed. The largest was 9 inches in diameter. In one of the three the pedicle was twisted and the patient presented the syndrome of an acute abdomen on admission. The other two complained of abdominal distention and discomfort. All complained of amenorrhœa for some time. All three had borne children. The first, three, the second, nine and the third, one. In the second the appendages on the opposite side were diseased. Ascites was present in one.

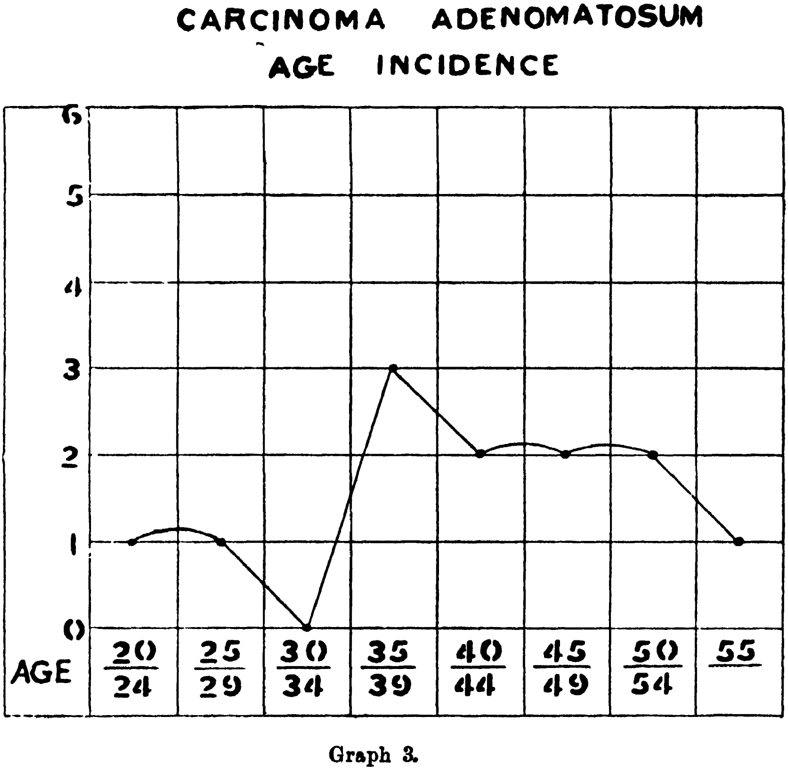
Age incidence:—The age of the patient was 40, 50 and 40.

Treatment:—Salpingo-oophorectomy was performed in all. There was not much post operative disturbance and the convalescence was uneventful.

CARCINOMA ADENOMATOSUM

There were twelve tumours in my series that belonged to this group. Five were bilateral and seven unilateral. The largest tumour filled the whole abdominal cavity and the smallest the size of a grape fruit. In five patients the tumours were bilateral.

Age incidence:—The youngest patient was 20 and the oldest 55. Graph 3 illustrates the age incidence.



Graph 3.

Menstrual and Obstetric Histories:—The patient aged 20 menstruated regularly but menstruation was irregular and scanty in all the patients between the ages of 35 and 40. One, aged 40, had menorrhagia and the remaining menopausal amenorrhœa. Two patients were unmarried, four were sterile and six bore children (from one to four).

Symptoms and complications:—Emaciation and cachexia was noted in five only. The majority complained of abdominal pain of varying intensity. Three complained of disturbance of micturition. One with bilateral tumours had pyelitis, *vide* fig. 5. Ascites was noted in five.

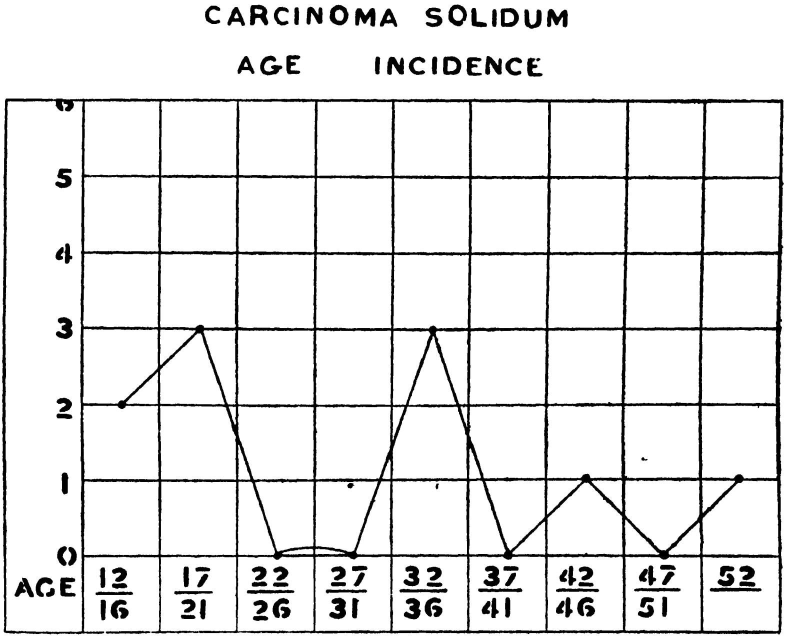
Treatment :—Oophorectomy, unilateral or bilateral was performed in six. In two cases only partial excision was possible and in four panhysterectomy was performed. After the pathological examination of the specimens removed, all the patients were subjected to Deep Therapy treatment.

Operative Mortality :—Two patients died, one in whom partial excision was done and one other in whom panhysterectomy was performed.

CARCINOMA SOLIDUM.

This is an interesting group. although consisting of 10 cases only. The youngest patients in this group were (a) 12, (b) 16 and (c) 17 years of age. (a) Had not yet menstruated, nor showed sign of any advent of puberty (Fig 6). The other two (b) and (c) were fully developed and menstruated at 13 and 14, respectively, but complained of scanty menstruation for the last six months. (c) Was operated by a general surgeon for a solid tumour of the right ovary, the size of an orange, 8 months before her admission to my Hospital.

The oldest patient in this group was 52. The largest tumour was the size of 6 months pregnant uterus and the smallest, the size of a turkey egg. Graph 4 illustrates the age incidence.



Graph 4.

Menstrual and obstetric histories:—Three patients were unmarried and one a child widow. Four patients complained of amenorrhœa of varying periods, from 2 months to two years. Besides the three youngest patients mentioned above one complained of profuse periods, one of menopause and another had normal periods. Six patients were married and of these four were sterile.

Symptoms and complications:—Abdominal pain was complained by six patients, and abdominal swelling by four. Ascites was present in five cases and disturbance of micturition in four. Oedema of the legs was noted in two.

The tumours were bilateral in four cases.

Treatment:—In four cases the operation had to be abandoned after partial excision of the growth. In four panhysterectomy was performed and in two bilateral oophorectomy only, because of extensive pelvic metastasis.

Regional and pelvic glands were involved in five cases.

Immediate results:—Two patients died in the Hospital, one in three weeks of the operation and the other 54 days after. All others were treated with deep therapy and dicharged.

In a cosmopolitan City like Bombay, where patients from all places come for treatment, it is very difficult to trace the patients after their discharge from the Hospital. Only three out of the eight that were discharged responded to the questionnaire and are fairly well for the last three years. Two aged 20 and one 32 at the time of the operation.

I presume that the age incidence of carcinoma of the ovaries in India has not yet been investigated. After reviewing the literature in my possession, I come across only one case reported by Gupta of Calcutta, in a married woman of 18 years, a case which was treated for tuberculosis of the pelvic organs and which only at the autopsy revealed the diagnosis of Carcinoma of the ovary. Probably many more cases remain unnoticed as they do not get into Hospital in time or are treated by 'Vaidyas' and 'Hakim.' Moreover, it is now very difficult to get an autopsy, because of religious and other reasons, and obtain a definite pathological diagnosis of the unoperated tumours. The case of Miss (a) aged 12 merits special mention. She was transferred from the medical wards of the K. E. M. Hospital to my gynæcological wards, for a swelling of the lower abdomen. She was admitted to the medical wards for malaria from which she suffered for two months. On admission, the girl was extremely emaciated and presented a cachectic appearance. There was no temperature now, but her general condition was very poor (Fig. 6). The spleen was enlarged and there were occasional bouts of cough. A few pus cells and R. B. Cs were found in the catheter specimen of the urine. X-Ray of the lungs showed nothing of importance. She had not yet menstruated, nor were there signs of puberty. She stated that her abdomen had grown rather quickly for the last two months. A pyriform swelling was seen rising from the pelvis to about 2 inches below the umbelicus. It was hard and irregular in contour.

Vagina:—Virgo intacta-P. R. (per rectum) The cervix was felt high up at the level of the symphysis pubis, hard but small, directed towards the hollow of the sacrum. An irregular, nodular and hard mass was felt continous with the cervix filling the pelvic cavity and rising to about 2 inches below the umbelicus; the mass could be moved somewhat from above downwards, but not from side to side. There was no infiltration around the rectum nor the bladder seemed to be involved.

From the physical signs the tumour appeared to be uterine and a provisional diagnosis of a sarcoma of the uterus was advanced. At the Laparotomy the swelling was found central and very vascular, it bled on slight provocation. It was difficult to locate the uterine body or the appendages. After a careful search the round ligaments were identified and a rapid side to side Hysterectomy attempted (Kellys). The tissues were friable and the bleeding very free. However, the mass was removed *in toto.* The peritonisation was difficult and the oozing free. A firm gauze pack was left in the pelvis and the abdomen closed. The patient survived the operation, but died of cachexia and exhaustion on the 54th day of the operation.

The pathological report of the specimen was " solid carcinoma of the ovary ".

The autopsy. At the autopsy, the pelvis was found invaded with secondary growths and the cervical stump revealed that a hysterectomy was really performed. The left ovary was found in the Dougla's Pouch enlarged, the size of a tangerine orange, and carcinomatous. The ureters were wide, dilated and the kidneys full of pus. Secondary deposits were found in the liver, spleen, mesenteries and lungs. The immediate cause of death was pyelitis. The case offers some peculiarities of interest :—

1. The growth in the right ovary had burried the uterus, so as to distort its anatomy and be mistaken for uterine tumour.

2. The invasion of the left ovary appears to have been slower or subsequent to the operation.
3. Menstruation had not been stablished, nor any feminine characteristics of puberty had appeared.
4. X-Ray investigations failed to detect any secondary dissemination although the growth was extensive.
5. The absence of ascites or oedema of the legs.
6. The ultimate infection of the kidneys and stricture of the ureters.

CARCINOMA PAPILLOMATOSUM

There were only five cases in my series. The largest tumour was the size of a cocoanut and the smallest the size of an orange.

Age incidence. The youngest patient was 21 years of age and the oldest 45.

Menstrual and Obstetric Histories. Menstruation was normal in two cases. One patient complained of dysmenorrhœa and two of amenorrhœa. All the five patients were married, two, one of 21 and the other of 45, were sterile.

Symptoms and complications. A dull abdominal ache was complained by all five. One complained of abdominal distention and had ascites, one of severe dysmenorrhœa. She was 21 years of age and sterile. In one case the tumour was bilateral, but she had 4 children. Peritoneal metastases was found in three cases.

Treatment. Panhysterectomy was performed in one case and Oophorectomy in others. There was no mortality in this group. All were subsequently treated with Deep Therapy.

CYSTADENOMA PSEUDOMUCINOSUMS WITH SECONDARY MALIGNANT CHANGES.

Only two cases could be included in this group. In one case the growth was bilateral and in the other unilateral. The age of the patients was 19 and 35 respectively. The first had scanty menses and the second amenorrhœa. Both bore children.

Treatment. Oophorectomy was done in both and subsequent deep therapy treatment was given.

FIBROMA

Only three cases were met. The largest tumour was the size of foetal head and the smallest of Tangerine orange.

The ages of the patients were 17, 34 and 45. The youngest of the three was unmarried. The tumors were unilateral in all the three patients. The first complained of scanty menses, the second of amenorrhœa for four months, and the third amenorrhœa for two years. The first had two children, the second nine children and the third was unmarried.

Treatment. Oophorectomy was undertaken in all the three cases.

DERMOIDS.

There were four dermoid tumours. The largest was the size of a big cocoanut and the smallest the size of a Duck's egg. The youngest patient was 33 years of age and the oldest 50.

All had regular menstruation except one of 50 years of age, who complained of menopause. All bore children ; 2, 4, 4 and 7, respectively.

FIMBRIAL CYSTS.

These cysts were met four times. The largest tumour was the size of an orange. The ages of the patients were 17, 18, 29 and 35. The first was unmarried and was admitted for menorrhagia. The pedicle of the cyst was found twisted at the operation. The other three menstruated regularly.

In all cases the cyst could be dissected out.

CHOCOLATE CYSTS

This was an unique case. She was an unmarried woman of 29 and complained of dysmenorrhœa and menorrhagia. The tumour was the size of an orange. Oophorectomy was performed.

A large number of my cases were subjected to cystodiaphanoscopy (Transillumination) and translucent, opaque and solid tumours were differentiated before the operation. Figs. 5, 8, 9 and 10 illustrate some of the findings.

CONCLUSIONS.

1. A statistical and clinical study of a consecutive series of 126 ovarian neoplasms is presented.
2. The youngest patient in the series was of 12 years of age and the oldest of 60.
3. The gross incidence of malignancy in the series was of 23.01%.

4. The youngest patient suffering from carcinoma of the ovary was 12 years of age.
5. The gross operative mortality was 7.14%

Before concluding, I desire to express my thanks to Professor V. R. Khanolkar, the Chief of the Pathological Department of the K. E. M. Hospital and to Dr. R. G. Dhayagude, the Deputy Chief, for their valuable assistance and to my colleagues Drs. Purandare and Miss P. C. Daroowalla for their consent to utilize some of their cases to complete my consecutive series of 126 cases of ovarian neoplasms.

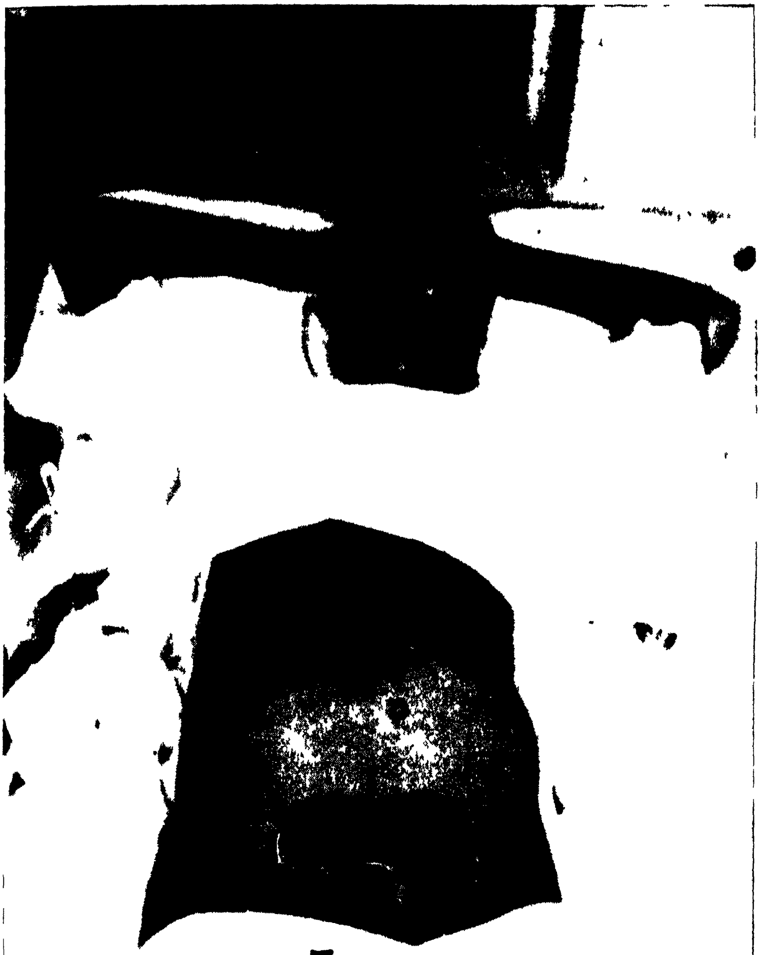


Fig. 5

Carcinoma Adenomatosum Bilateral.

Cystodiaphanoscopy—only the bladder is lighted bright red. The tumour is not at all transluent.

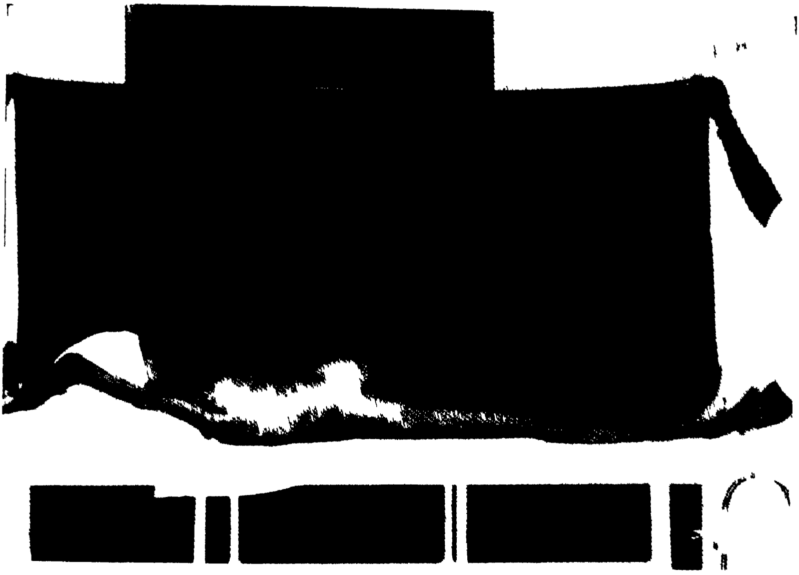


Fig. 6

Fig. 7

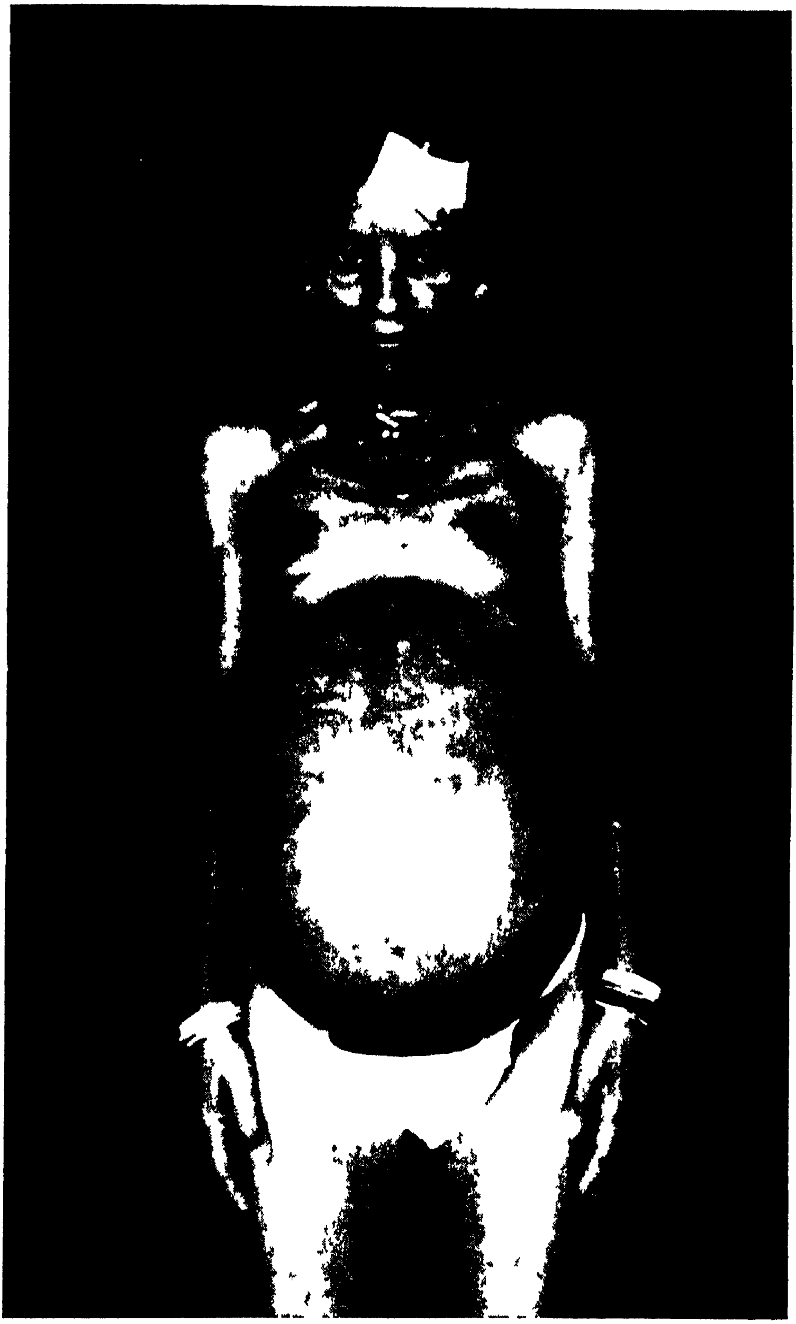


Fig. 8

Cystadenoma Pseudomucinosum undergoing malignant changes

Cystodiaphanoscopy shows only the bladder lighted bright red. The Tumour is opaque

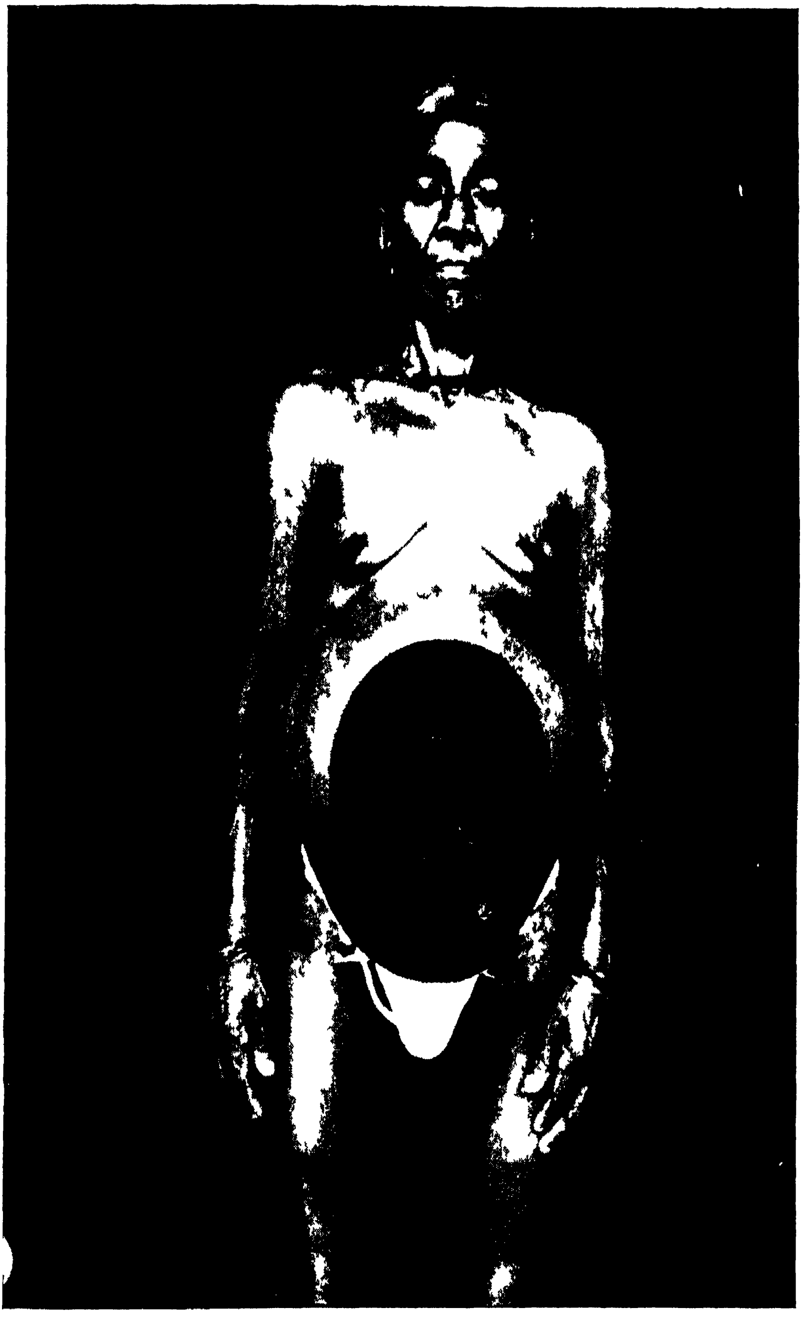


Fig 9

Cystoma Simplex Serosum

Cystodiaphanoscopy shows the bladder lighted bright red and the Tumour like a Chinese lantern

THE EXCRETION OF VITAMIN C IN URINE AND THE STATE OF SATURATION IN NORMAL INDIVIDUALS IN BOMBAY.

By

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The diseases arising from vitamin deficiency are avoidable and an early diagnosis to a predisposition to avitaminosis can be ascertained by certain well known tests. Of all the known vitamins the subnutrition of vitamin C is more easily detectable. The manifest disease due to lack of this vitamin is scurvy. Though now-a-days it is indeed very rare to see a typical case of scurvy due to complete deprivation of vitamin C, yet there are manifest symptoms of a deficiency of vitamin C intake. Plimmer has recently summarized these as: " Before definite symptoms of scurvy appear, there is a period of ill health characterised by certain symptoms which may also be looked for in those who habitually take too little vitamin C though they get enough to prevent acute scurvy. These symptoms are a sallow, muddy complexion, loss of energy, fleeting pains in the joints and limbs especially in the legs, usually mistaken for rheumatism. So called rheumatism in infants and young children has often been proved to be due to insufficient vitamin C and is really scurvy. '

Vitamin C plays an imporant role in the economy of the human body and is of paramount importance to the physiologist, pharmacologist and the pathologist. It has been shown by Gothlin (1931) that vitamin C controls the capillary resistance and he has developed a test known as the "Capillary Resistance Test" by means of which vitamin C subnutrition can be detected by the number of petechial hæmorrhages that occur in the skin area when subjected to a sustained pressure of 50 mm. of mercury for 5 to 15 minutes.

Percy Howe (1926) in America and Zilva (1935) in England showed that deficiency in vitamin C is responsible for tooth defects and tooth decay.

The work of Findlay (1923) has shown that long continued low intake of vitamin C increases the incidence of infectious diseases.

King and Manten (1935) have shown how a body well saturated with vitamin C can withstand the onslaught of diphtheria toxin.

From the pharmacological point of view Hans Kreitmar

(1934) has shown a regenerative action of vitamin C on the blood of cats rendered anaemic by saponin. It does increase the antianaemic liver factor. Zilva and Johnson (1934) have shown that a normal individual under usual dietary condition excretes in the urine ascorbic acid in amounts dependent to a large extent on the amount of vitamin C habitually ingested. From their observations they concluded that the body is able to store up vitamin C until the tissues become saturated. Before saturation the vitamin C excretion was far less than when the body was saturated. Once the body was saturated the output was increased and maintained so long as the intake continued.

Harris and Ray (1935) have suggested that the estimation of ascorbic acid in the urine of the individual under his usual dietary condition or by noting the response to a test dose of vitamin C can be utilized for the assessment of the state of vitamin C nutrition of that individual.

The test suggested by them has been employed to find out vitamin C nutrition in Madras by Ranganathan and Sankaran (1936) and in Calcutta by B. Ahmad (1936). Since no work has been done in this part of India, we thought it worth while to undertake the study of vitamin C nutrition in Bombay.

TECHNIQUE

The estimation of vitamin C in the urine was carried out by the method of Harris and Ray and Ward (1933) which is a modification of Tillman's 2 : 6 dichlorophenol-indophenol method. Two twelve hours' samples were collected to include the 24 hour voidings, and titrated against the dye. For the preservation of ascorbic acid in the urine, glacial acetic acid was added to make the total concentration 10 per cent acid and the samples were collected in dark coloured bottles. All the necessary precautions for titrations were taken and each titration was completed within two minutes to prevent the reduction of the dye by reducing substances other than ascorbic acid. A 24 hour excretion of vitamin C of every individual was found twice at an interval of 15 to 25 days and the mean of the two readings was taken as the average excretion for the individual.

About 107 subjects were submitted to the urine analysis test and these were divided into 2 groups *viz.* A and B. Group A consisted of students, members of the staff, research workers and laboratory assistants who were about 77 in number. Group B consisted of members selected from the Industrial Home, Matunga and were 30 in number. This division in groups A and B was necessary from a dietetic point of view, because Group B is supplied with a known constant quantity of vitamin C from day to day, while the vitamin C ingestion of group A may vary from day to day or may be constant as in Group B. The group "A" was further divided into males and females. Group B needed no subdivision as all the members were males.

The minimum, maximum and average excretion of vitamin C of Groups A and B expressed in milligrams is given in table No. 1.

Ranganathan and Sankaran's figures (*loc. cit.*) for Madrasis varied from 4·75 to 8·65 mgms. per day.

TABLE NO. I

Excretion of Vitamin C in mgms. in 24 hours

Group A		*Excretion of Vit. C in mgms.*	
Males ...	Max.	27·69	Observations 47.
	Min.	9·15	
	Mean.	15·80	
	σ =	± 3·10	
Females ...	Max.	16·40	Observations 30.
	Min.	6·69	
	Mean.	11·17	
	σ =	± 2·09	
Group B			
	Max.	34·31	Observations 30.
	Min.	7·41	
	Mean.	21·75	
	σ =	± 4·40	

B. Ahmad (*loc. cit.*) obtained figures for Bengalis which varied from 23 to 35 mgms. per day.

From the above figures worked out for the excretion of normal individuals we get only an approximate idea regarding the state of body saturation with vitamin C because if a person saturated is receiving for some time a diet low in vitamin C, the rate of excretion would fall and yet the body tissue for the time being would remain in a state of saturation. The study of vitamin C nutrition of an individual is therefore not complete until we determine the state of saturation of the body or employ the saturation test, for almost all the workers on this subject are convinced that it is more accurate than the estimation of daily ascorbic acid excretion in the urine. Unsaturation is not an abnormal state and occurs in normal individuals. This may be termed a subclinical vitamin C deficiency and is in most cases due to general dietary deficiency.

There are various tests for estimating the state of saturation *viz.* (1) Gothlin's Capillary Resistance Test (*loc. cit.*), (2) Rotter's Intradermal Test (1937), (3) The Ascorbic Acid Saturation Test in which a known quantity of ascorbic acid is administered either orally or intravenously, and (4) The Plasma Ascorbic Acid Determination Test (Pijoan and Klemperer 1937).

In this investigation the ascorbic acid saturation test by administering a known quantity intravenously has been used. The intravenous administration eliminates the factor of variability in absorption or in destruction in the gastro-intestinal tract. The method adopted is that described and used by Phillip Finkle (1937) with some modifications.

Finkle's method is as follows :—On the day of the test the subject is permitted to have his or her usual meals with the exceptions of citrus and other food containing vitamin C. There is no restriction of fluids. The urine is collected at about 9 a.m. and 11 a.m. and the vitamin content is determined in each specimen. After the 11 a.m. voiding, 100 mgms. vitamin C is administered intravenously. The subject is requested to void only at about 1-30, 3-30, 5-30 p.m. respectively and the vitamin C content is again determined by 2 : 6 dichlorophenol-indophenol method as used by Harris and Ray and Ward (*loc. cit.*). Since normal subjects were studied no dietary restrictions were placed upon them other than those stated above. The rationale of the test is that the excretion of vitamin C per millilitre must rise by about 4 to 8 times the values found before the injection if the subject is saturated. The total 24 hour output rises to 45 to 65 mgms. vitamin C. In cases of unsaturation the individual voidings contain less than 3 mgms. and the total output for the 24 hour period is considerably below the normal levels. When there is no acute rise in excretion following the intravenous administration of vitamin C, the total output for the 24 hour period remains at about the same low level as previous when no vitamin was injected. It was therefore considered unnecessary to continue to measure the total excretion of vitamin C for the entire 24 hour period. It is observed that the excretion of vitamin C rises within about 2 hours to about 5 to 6 times the values found before injection.

Besides the comparison of the percentages of vitamin C excreted before and after the test dose, it was thought worthwhile to compare the actual quantity of vitamin C excreted in 5 to 6 hours after the test dose, because it was possible that the percentages may vary according to the intake of liquids by the individuals.

TABLE NO. II
RESULTS OF THE TEST DOSES.
(Expressed in absolute quantities in mgms.)

No.	Name.	Group.	Total Excretion of Vit. C. in 24 hrs. mgms.	Average excretion per voiding before T.D. mgms.	Excretion of Vit. C in first voiding after T.D. (2½ hrs) mgms.	Excretion of Vit. C. in the second voiding after T.D. (5 hrs) mgms.	Total excretion in 5 hrs. after T.D. mgms.
Males							
1	A. F.	A	18.50	2.05	5.05	3.46	8.51
2	V. N. P.	,,	27.69	1.73	28.92	20.77	49.69 S
3	D. R. S.	,,	10.30	4.80	2.94	2.88	5.82
4	B. N.	,,	14.53	3.24	2.05	2.11	4.16
5	A. G. B.	,,	10.72	1.50	1.92	2.06	3.98
6	S. V.	,,	15.76	1.78	3.09	4.04	7.13
7	P. L. P.	,,	13.86	0.86	3.70	1.57	5.27
8	D. A. D.	,,	15.31	1.67	6.64	4.39	11.03
9	S. N. N.	,,	14.37	10.05	55.58	36.66	92.24 S
10	A.K.B.B	,,	13.41	7.42	61.53	14.81	76.34 S
11	H. M. B.	,,	18.60	2.25	5.48	2.50	7.98
12	R. G. C.	,,	22.34	1.04	4.00	1.40	5.40
13	J. D. R.	,,	15.54	1.63	3.12	2.85	5.97
14	B. V. D.	,,	16.91	1.24	6.66	8.00	14.66
15	E. R. D.	,,	16.30	3.50	5.33	11.75	17.80
16	B. N. A.	,,	20.50	0.95	7.10	5 00	12.10
17	E.R. Dm.	,,	19.75	3.39	6.66	16.66	23.32
Females							
18	K. D. P.	,,	8.59	0.95	1.81	1.53	3.34
19	D.B.L.	,,	9.70	0.98	2.85	2.43	5.28
20	F. H. B.	,,	8.28	4.85	53.38	26.66	82.04 S

TABLE NO. II—*concld.*

No.	Name.	Group.	Total Excretion of Vit. C. in 24 hrs. mgms.	Average excretion per voiding before T.D. mgms.	Excretion of Vit. C. in first voiding after T.D. (2½ hrs). mgms.	Excretion of Vit. C. in the second voiding after T.D. (5 hrs). mgms.	Total excretion in 5 hrs. after T.D. mgms.
Females							
21	I. A.	A	10.58	1.98	4.00	2.66	6.66
22	P. M. N.	,,	13.00	0.42	5.30	3.63	8.93
23	S. R. M.	,,	10.36	0.52	10.00	2.50	12.50
24	K. I. V.	,,	9.34	1.27	8.90	8.00	16.90
25	T.	,,	13.93	1.50	3.63	4.50	8.13
26	M. V. H.	,,	12.26	2.08	4.00	3.80	7.80
27	M. A.	,,	12.65	3.03	32.90	20.00	52.90 S
28	B. P.	,,	8.43	1.16	3.22	1.66	4.88
29	S. R. D.	,,	11.83	1.25	3.07	1.08	4.15
30	A. Y. H.	,,	12.88	1.30	3.20	1.21	4.41
31	M. I. J.	,,	11.70	0.52	7.14	11.76	18.90
Males	*Group B.*						
32	S. M.	B	24.80	4.23	28.57	21.42	49.99 S
33	T. B.	,,	12.99	0.94	2.80	5.28	8.08
34	N. I.	,,	26.93	3.34	3.08	1.50	4.58
35	P. R.	,,	29.37	4.06	5.16	5.83	10.99
36	M. H. A.	,,	11.41	0.83	11.11	8.42	19.53
37	K. P.	,,	18.82	1.23	26.66	28.57	55.23 S
38	M. K.	,,	7.45	0.40	14.00	10.00	24.00
39	A. F.	,,	34.31	5.42	32.00	34.78	66.78 S
40	A.R.S.D.	,,	17.42	4.00	10.00	13.13	23.13

S = Saturated person.

TABLE NO. III.

RESULTS OF TEST DOSES.

(Expressed according to the percentages).

No.	Name.	Excretion 24 hrly Mean in mgms.	Before Dose % average.	1st sample After dose %	2nd sample after Dose %	Total 5 hrly Vit. C Excretion mgms.
	Males.					
1	A. F.	18.50	0.97	5.61	6.52	8.51
2	V. N. P.	27.69	3.72	17.17	13.84	49.69
3	D. R. S.	10.30	3.41	3.92	5.05	5.82
4	B. N.	14.53	3.16	2.73	1.76	4.16
5	A. G. B.	10.72	1.74	0.91	2.42	3.98
6	S. V.	15.76	2.76	5.62	8.08	7.13
7	P. L. P.	13.86	2.95	3.77	2.12	5.27
8	D. S. A.	15.31	2.01	7.63	4.88	11.03
9	S. N. N.	14.37	10.69	73.86	66.55	92.24
10	A. K. B. B.	13.41	13.80	16.67	30.85	76.34
11	H. M. B.	18.60	1.42	3.65	3.00	7.98
12	R. G. C.	22.34	1.95	3.20	1.47	4.40
13	J. D. R.	15.54	3.84	7.80	10.10	5.97
14	B. V. D.	16.91	1.45	3.80	5.33	14.66
15	E. R. D.	16.30	2.00	7.10	11.75	17.80
16	B. N. A.	20.50	2.00	3.10	1.66	12.10
17	E. R. Dm.	19.75	1.69	7.40	7.75	23.32
	Females.					
18	K. D. P.	8.58	1.49	3.17	5.10	3.34
19	D. B. L.	9.70	3.86	4.75	4.41	5.28
20	B. F. H.	8.28	11.97	79.11	76.17	82.04

TABLE NO. III—*concld.*

No.	Name.	Excretion 24 hrly Mean in mgms.	Before Dose % average.	1st sample After dose %	2nd sample after dose %	Total 5 hrly Vit. C Excretion mgms.
21	S. I.	10.58	2.43	5.73	7.60	6.66
22	P. M. N.	13.00	2.88	21.20	18.15	8.93
23	S. R. M.	10.36	0.93	17.24	8.96	12.50
24	K. I. V.	9.34	2.68	25.42	7.27	16.90
25	V. T.	13.93	1.99	1.65	3.00	8.13
26	M. V. H.	12.26	3.23	4.44	4.75	7.80
27	M. M.	12.65	3.03	73.11	50.00	52.90
28	B. P.	8.43	1.42	1.95	3.23	4.88
29	S. R. D.	11.83	2.42	6.14	1.80	4.15
30	A. Y. H.	12.88	1.24	7.10	1.86	4.41
31	M. I. J.	11.70	0.93	10.20	11.76	18.90
	Group B Males					
32	S. M.	24.8	4.51	16.76	20.40	49.99
33	T. B.	12.99	0.93	0.46	1.32	8.08
34	N. I.	26.93	2.05	1.92	1.20	4.58
35	P. R.	29.37	0.66	2.95	2.01	10.99
36	M. H. A.	11.41	1.14	5.55	5.61	19.53
37	M. H.	7.45	1.17	4.51	4.76	24.00
38	K. P.	18.82	1.51	8.16	8.47	55.23
39	A. F.	34.31	1.34	6.40	6.62	64.78
40	A. R. S. D.	17.42	1.00	2.50	3.28	23.13

In Table Nos. II & III are given the results both in absolute quantities of vitamin C and the percentage concentration before and after the test dose. The state of saturation was judged according to Barron et al (1938). It was presumed that those excreting less than 5–10 mgms. in five hours after the test doses were unsaturated. Those excreting 10–20 mgms. in five hours were on the border-line of saturation and those excreting above 25 mgms. were saturated.

DISCUSSION

In group A the majority of the subjects selected for the investigation belong to the middle class of the population who could grasp the significance of the problem. Their day to day diet though in some cases possibly low in vitamin C owing to want of fruits and green vegetables was fairly nutritious and they appear to be all healthy and hence were taken as normal individuals.

The volume of urinary excretion for 24 hours in men varied frow 650 to 3000 cc. with an average of 1400 cc ; while in women it varied from 360 to 2100 cc. with an average of 890 cc. It was found that in summer the quantity was rather low and was largely dependent on the intake of fluids.

The excretion of vitamin C in men varied from 9.15 mgms. to 27.69 mgms. the average being 15.80 mgms. In females it varied from 6.69 to 16.4 mgms. and the average was 11.17 mgms.

From the figures it could be seen that in no case was the excretion of vitamin C as low as 2 to 3 mgms. as is reported by Ranganathan and Shankaran (*loc. cit.*) in their investigation in Madras on people other than soldiers and Sikhs. This is possibly due to the fact that our subjects in the present investigation belong to a better class of people whose diet probably was not so low in vitamin C. The excretion in women was lower than that in men. No suitable explanation could be found. It was, however, occasionally found that the vitamin C excretion (as judged by the dichlorophenol-indophenol test) in some women was unconceivably high varying from 50 to 150 mgms. per day. On inquiry it was learnt that such subjects at the time of urine examination were drawing near to their menstrual period. The possible explanation for this increase may be due to some bodies at this period excreted in the urine which could reduce the dye or it may be that the rapid disintegration of the Corpus Luteum was responsible for the extra amount of ascorbic acid found in the urine as it is well known that Corpus Luteum acts as a store of vitamin C. Nothing definitely can be said at this stage and it is intended to pursue the investigation to throw further light on the subject.

In group B subjects belonged to an industrial school where the dietetic conditions were strictly controlled in connection with a nutritional research. All the boys received about 80 to 100 mgms. of vitamin C in raw rations in their daily diets although the nutritive value of the diets differed in other constituents. The excretion of urine in this group varied from 670 to 3000 cc. with an average of 1800 cc. The excretion of vitamin C varied from 7.44 to 34.31 mgms. the average being 21.75 mgms. The group B was specially selected to note the level of excretion of vitamin C if a fairly good supply of vitamin was given and this could be said to be approximately the optimum level of excretion when diet contained enough vitamin C. The figure 21.75 mgms. average closely agrees with that reported by Harris and Ray, Finkle, and Portnoy and Wilkinson (1938) for a fairly saturated person. It should be mentioned incidentally that the subjects from group B were receiving the diet for sufficient length of time to overcome the previous subnutrition if any.

TEST DOSE

That the estimation of total excretion of vitamin C in urine for twenty four hours gives a fairly good idea of the state of saturation is beyond doubt (Harris and Ray *loc. cit.*). But the absolute state of tissue saturation could only be determined by the employment of certain tests such as (1) the intravenous injection of a known quantity of vitamin C, (2) the estimation of plasma vitamin C level test, (3) the capillary resistance test of Gothlin. The first test was thought to be the most acceptable to the subjects and yields fairly accurate results. It was employed throughout the experiment. The test could not be carried out in all the 107 subjects, but some representative cases were selected (*i. e.* some excreting too low, some too high and some intermediate).

In group A it was found that cases Nos. (1, 12, 21, 22 etc.) in spite of high daily excretion failed to give indications of their being saturated. The findings are in agreement with those of Harris and Ray and Ranganathan and Sankaran. But in no case so far investigated was it found, that subjects having a low level of excretion were saturated. Thus it shows that a high level of excretion does not necessarily mean a state of saturation while a consistant low level of excretion definitely suggests a state of hypovitaminosis C. The above suggestion may not hold good in cases of persons who had received an enough supply of vitamin C in their diet, but prior to their test the vitamin C content of the diet has fallen considerably low.

In group B nine subjects were chosen, three excreting the highest, three excreting the lowest and three near about the mean. Here it was found that those excreting the maximum were saturated, the medium excreting people were on the border line of saturation, whilst those excreting low were unsaturated.

A question would arise as to why all the subjects in group B were not saturated. This could be explained on the assumption that this difference existed on account of the variability in the rate of absorption of vitamin C from the gastro-intestinal tract. Those excreting low vitamin C suffered from low rate of absorption probably more destruction of vitamin C in the alimentary canal. These subjects should be considered physiologically below par.

Out of 40 test doses given so far only 8 subjects were found to be saturated. On scrutinizing the data it can be seen that a state of under nutrition of vitamin C, not showing manifest symptoms of avitaminosis C, thus exists in this part of the country as elsewhere like Madras, Bengal and Western countries.

In all our actions the watchword is moderation, but considering the state of subnutrition in vitamin C prevalent in Bombay, it is safer to err on the wrong side of moderation and take a more liberal supply of vitamin C in the form of fruits and fresh green vegetables so as to keep our bodies if not over, at least saturated, as vitamin C helps to keep the body in good nutrition and in the apt phrase of McCollum and Simmonds (1929) leads to "the preservation of Characteristics of Youth."

SUMMARY.

1. 107 subjects were examined for their daily vitamin C excretion in urine and 40 were subjected to the test dose to find out the body saturation.

2. Daily excretion of vitamin C in males varied from 9.15 to 27.69 mgms. and females from 6.69 to 16.4 mgms.

3. In 30 subjects getting the liberal supply of vitamin C the excretion varied from 7·41 to 34·31 mgms.

4. Out of 40 test doses given, only 8 were found to be saturated and a state of subnutrition of vitamin C is observed in this part of the country as elsewhere.

5. In cases of females an abnormally high level of vitamin C excretion as judged by 2:6 dichlorophenol-indophenol test was observed towards the approach of menstrual period.

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THE SKELETON OF PERIOPHTHALMUS BARBARUS (LINN.)

II. BRANCHIAL ARCHES, VERTEBRAL COLUMN AND APPENDICULAR SKELETON

(*With 1 text and 4 plate figures*)

(Continued from Paper I of the series which appeared in Vol. VI, Part V of this Journal, March 1938.)

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THE BRANCHIAL ARCHES

The five pairs of branchial arches (Plate VI. Fig. 7, I. A. to V. A.) are articulated to form a flattened frame-work including the two pairs of tooth-bearing bony plates. This frame-work is situated behind and inside the hyoid arch and is jointed to it by a ligament from the middle of its ventro-anterior edge. The ventral side of this frame-work consists of one of these pairs of plates behind, and in front a chain of three basi-branchials (B. Br.) to whose sides are attached the five arches. The two anterior basi-branchials are elongated and rod-like with wing-like lateral expansions. The third and hindmost basi-branchial is a small rhomboidal bony plate providing articulation for the third and fourth arches. The dorsal side of the frame-work is shifted posteriorly and consists of two elongated plates to whose sides are attached the dorsal elements of the first four branchial arches. These plates (Sup. Ph.) are really formed by the fusion of the pharyngeal or the terminal dorsal elements of these arches. Very often the pharyngeal plate on each side appears to be divided into three pieces. The anterior piece is directed transversely and provides attachment to the epibranchials of the first and second arches. The middle piece forms the major part of the pharyngeal plate and is articulated to the epibranchial (E. Br.) of the third arch. The posterior piece is directed longitudinally and is jointed to the fourth and last epibranchial. The teeth on the first two pieces are in transverse rows and they get larger towards their median sides. The teeth on the third piece are small and crowded together.

The First Branchial Arch.—(Plate VI. Fig. 7, I. A.) This arch is V-shaped with its one arm being longer than the other. It is complete and has got all its bony parts present. It consists of three, mostly cartilaginous and strip-like bones joined together by intervening pads of cartilage. The first piece on the ventral side—the hyprobranchial (H. Br. 1) is short and plate-like with its anterior median corner bent downwards. It can be easily conceived to be formed from a rod-like piece by being much flattened at the ends, and produced into lateral expansions in the middle. It is attached anteriorly to the first basibranchial (B. Br.) and posteriorly to the ceratobranchial (C. Br. 1). The second piece—the ceratobranchial is the longest of these and consists of a slender bony rod with narrow lamellar projections on the sides. Anteriorly it is broad and flat but posteriorly it narrows to a bony rod. With its laminar projections it forms a groove for the attachment of the gill-rays and the lodgment of the branchial vessels. This bone is so turned in the middle that its groove is ventral anteriorly, and becomes directed outwards posteriorly. Its posterior end articulates with the dorsal epibranchial (E. Br. 1) through a flexible cartilaginous bent joint. The epibranchial is again a short rod-like bone bifurcated at its proximal end. Its anterior branch joins the anterior pharyngeal piece (Sup. Ph.) through a long strip of ligament and the posterior articulates with it directly.

The Second Branchial Arch.—(Plate VI. Fig. 7, II. A.) This is complete like the first. Its hypo-(H. Br. 2) and cerato-branchials (C.Br.2) are similar to those of the first, but its epibranchial (E. Br. 2) ends dorsally into a slender flattened rod which also articulates with the anterior pharyngeal piece. Ventrally the hypobranchial (H. Br. 2) articulates at the junction of the first and second basibranchials.

The Third Branchial Arch.—(Plate VI. Fig. 7, III. A.) This is also a complete arch. It has a broad but short hypobranchial (H. Br. 3) articulating with the second basi-branchial. Dorsally its epibranchial (E. Br. 3) articulates with the middle piece of the pharyngeal bone. Its ceratobranchial (C. Br. 3) resembles that of the second branchial arch.

The Fourth Branchial Arch.—(Plate VI. Fig. 7, IV. A.) It is incomplete as it has no distinct hypobranchial. It now consists only of two pieces, the cerato-(C. Br. 4) and the epibranchials (E. Br. 4) which resemble those of the previous arches. Its ventral extremity articulates with the third basibranchial and the dorsal with the posterior pharyngeal plate.

The Fifth Branchial Arch.—(Plate VI. Fig. 7, V. A.) The fifth arch is represented on each side by a ventral triangular plate already described in connection with the branchial frame-work. These two plates are situated very close together and are opposed by their median sides. They are loosely connected to the third basibranchial by their elongated anterior corners. These plates are produced on their ventral surfaces into small rounded vertical plates providing additional attachment for the muscles. Each of them bears usually seven rows of teeth on its dorsal surface. The teeth along their median sides are larger while those of the distal rows are smaller. They are just opposite the dorsal pharyngeal plates, and as they are pointed and the points turned backwards, they may be useful in preventing its prey from escaping out of the pharynx.

The Gill Rays. The gill filaments are supported by a series of very delicate, fragile gill rays. They are in two rows attached mostly to the ceratobranchials and very few to the hypo- and epibranchials. They are on the ventral side of the bones.

THE VERTEBRAL COLUMN.

The vertebral column of this fish (Fig. 8 and Plate VII. Fig. 9) consists of twenty-six vertebræ and is divided into a trunk and a tail region. The vertebræ of the trunk region can be generally distinguished from those of the caudal region by the presence of ribs (Rib.) in connection with the former and of hæmal spines (Plate VII. Fig. 9, H. Sp.) in the latter. But in this fish there are five vertebræ *i. e.* from the 10th to the 14th which show the characteristics of both the trunk and tail regions. The 10th vertebra has got ribs and its parapophyses (Par. F.) meet below to form the hæmal arch (He. A.). The vertebræ from the 11th to the 14th are more like the caudal vertebræ than the trunk and differ from them in possessing also pairs of simple ribs (Si. Rib.). As a matter of fact, all these vertebræ are taken as caudal ones by the systematists on account of their possessing hæmal arches. Accordingly the first nine vertebræ constitute the trunk region and the remaining seventeen form the caudal region.

The neural spines (N. Sp.) are of different lengths and have got different inclinations towards the posterior side. The first four are directed obliquely upwards but the next six are inclined more downwards. As we pass backwards this inclination gradually lessens. The 6th neural spine is the longest of all and the remaining become shorter and shorter both anteriorly and posteriorly. The first four hæmal spines are much inclined upwards but in the posterior region the inclination gradually lessens. The hæmal spines in the anterior region are long and become shorter towards the posterior end.

The Curvature:—The vertebral column is not straight throughout its length. Its anterior third part extends obliquely downwards towards the middle of the body and is situated above its spacious abdominal cavity. Then it continues as a straight column, but in its middle third it appears to be slightly shifted towards the ventral edge while in the posterior third it is midway between the two edges.

The vertebræ are amphicœlous as in other fishes, but their anterior and posterior conical excavations are generally unequal in size, the anterior cavity being shorter and smaller than the posterior. These cavities are connected by a pin-hole canal situated in the narrow waist of the centrum. As in forming the vertebral column the anterior ring like face of a vertebra articulates with the similar posterior face of the preceding vertebra, a spindle-shaped cavity is enclosed between them. These intervertebral cavities and the pin-hole canals connecting them are filled with the remains of the notochord. Thus the latter is present inside the vertebral column throughout its length, but it is constricted intravertebrally in the region of the pin-hole canal.

The succeeding detailed description of the different types of vertebræ met with in the vertebral column of this fish is based on the study of specimens two inches in length which is the average length of fully developed specimens.

(i) *The First Vertebra :*—The first vertebra (Plate VII. Fig. 9,) is obviously shorter than the other trunk vertebræ and differs from the rest in many respects. It has no parapophyses, but from the antero-ventral side of the centrum a small bony plate projects downwards. Its neural arch (N.A.) is wider than its centrum (C.) and is as long as the latter. The two halves of the neural arch meet only at the base of the neural spine which arises at the extreme posterior end of the neural arch. The wide gap in front of the neural spine is covered in the living condition by a tough membrane. Its lateral bony wall contains a large foramen (F. Sp. N.) for the exit of the first spinal nerve. Its posterior margin does not bear zygapophyses and is obliquely truncate. The neural spine is formed of right and left neural processes and is more or less cylindrical. At its base a small round bony plate projects posteriorly. Its pointed end has also two narrow and thin bony projections along its anterior and posterior edges.

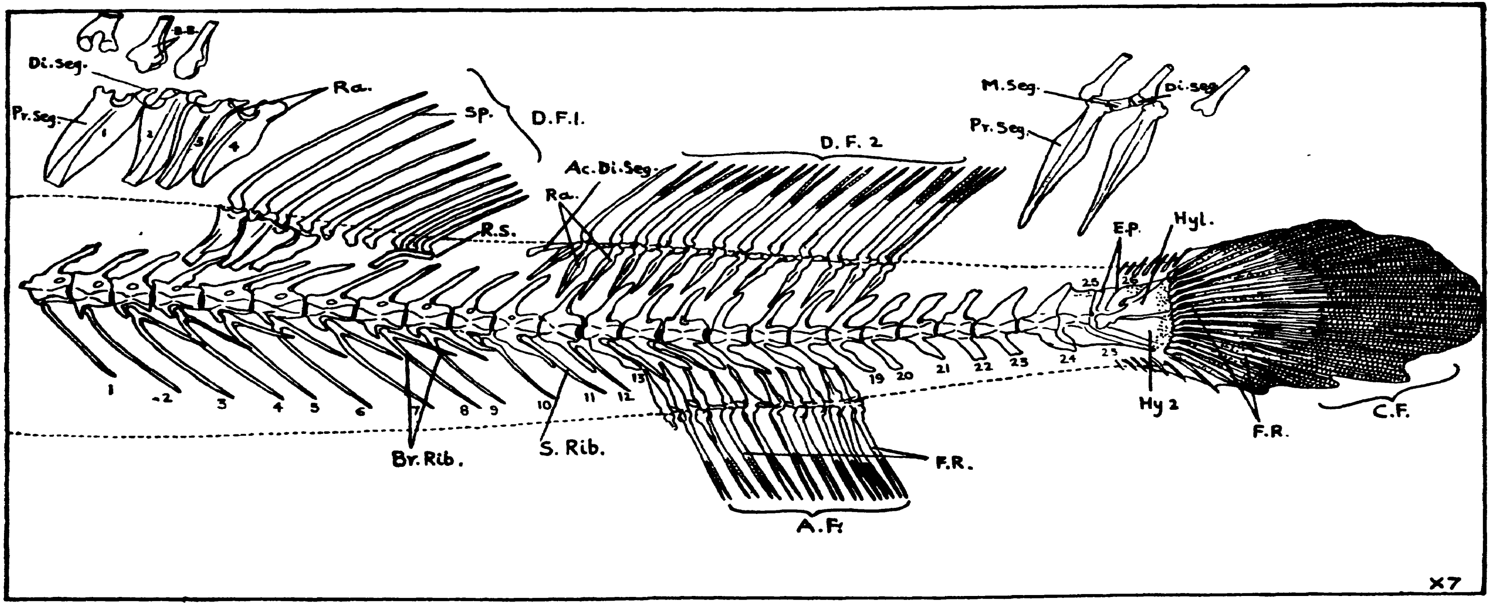

FIG. 8

Vertebral Column with the Skeleton of Median Fins.

Ac. Di. Seg. = Accessary distal segment ; A. F. = Anal fin; B. B. = Bifurcated base ; C. F. = Caudal fin ; D. F.$_1$ = Dorsal fin (first) ; D. F.$_2$ = Dorsal fin (second); Di. Seg. = Distal segment ; Ep. = Epural bones; F. R. = Fin rays ; Hy$_1$. = Hypural (first) ; Hy$_2$. = Hypural (second); M. Seg. = Middle segment; Pr. Seg. = Proximal segment; Ra. = Radial; R^5. = Fifth radial, S. Rib. = Simple rib ; Sp. = Spine.

The circular bony rim of the anterior face of its centrum articulates with the circular margin of a similar cavity on the posterior face of the basioccipital (Plate IV. B.O.). Similarly the neural arch also gives out on each side a strong bony process (Pr.) which bears an oval cartilage-capped facet (Fa.). The latter articulates with the corresponding facet on the exoccipital (Plate IV. Fa Ex. O.). Through these three articulations the vertebral column becomes strongly and immovably jointed to the skull.

(ii) *The Trunk Vertebræ* (Fig. 8 and Plate VII. Fig. 9). The vertebræ of the trunk region are more or less alike. But as we pass backwards they gradually appear to become longer and this increase is due to the elongation of the part of the centrum posterior to the pin-hole canal. As in the first vertebra the neural arches are open above for their greater length and covered only at the base of the neural spines. They do not bulge out as in the first vertebra but their lateral bony walls are more or less vertical. Posteriorly they are not produced into any dorsal articulating processes but appear to be reduced and rounded. Their anterior margins in the 2nd, 3rd and 4th vertebræ have got slight projections which are looked upon as the vestiges of anterior zygapophyses. Other vertebræ have got neither the anterior nor the posterior zygapophyses. The lateral bony walls of a neural arch are perforated by large foramina (F. Sp. N.) which are seen to be gradually shifting towards their dorsal margins. The inclinations and the lengths of neural spines have been already noted in the description of the vertebral column. The spines are not cylindrical as in the first, but are antero-posteriorly compressed and look like elongated, narrow and pointed blades. The terminal and median bony projections on the neural spines are usually absent.

The rod-like parapophysis (Parf.) present on either side of each vertebra originates near the anterior end of the centrum and is supported by a triangular bony plate or a supporting ridge extending from its base to the posterior end of the centrum. These parallel ridges are seen to get together in the successive vertebræ.

Thus in the 9th vertebra there is a single median plate or ridge which being narrow, hardly affords any support to the parapophyses. This ridge appears mainly to strengthen the centrum in the region of the pin-hole canal. In the first two vertebræ the parapophyses extend horizontally outwards, and in the succeeding vertebræ they are directed downwards, and extend obliquely outwards and backwards. In the last two vertebræ they are turned vertically downwards. In the anterior region they are short and become longer in the succeeding vertebræ towards the caudal region.

(iii) *The Caudal Vertebræ.* (Fig. 8 and Plate VII. Fig. 9). The first caudal or the 10th vertebra differs from the rest in not having a hæmal spine. But its hæmal arch formed by the union in the middle of the two parapophyses has got two short processes diverging from its ventro-lateral edges. As mentioned above the bony plates or the supporting ridges have become median and support only the waist of the centrum.

The next ten vertebræ are almost alike except in some minor details. The neural and the hæmal spines of these vertebræ become gradually shorter and more and more compressed laterally. From the 20th vertebra they appear blade-like. The foramen on the lateral wall of the neural arch gradually shifts towards its dorsal margin and in the 15th vertebra (Plate VII) there appears a notch in its dorsal edge. The hæmal spines of the first few vertebræ are much inclined backwards and are curved and cylindrical. The pin-hole canal comes to be placed midway between the anterior and posterior edges of the centrum. The median supporting ridge is present in some anterior vertebræ but in the last few vertebræ it is replaced by two narrow ventro-lateral ridges. In the posterior few vertebræ, the neural spine does not arise in the posterior region but its origin is seen to be gradually shifting towards the anterior side.

The neural spine of the 25th vertebra (Plate VII) is greatly compressed. Its hæmal spine also is similarly compressed and consists of a shaft behind, and a lamina in front. This expanded hæmal process articulates with the ventral edge of the lower hypural bone and forms the ventral edge of the strong median bony plate supporting the caudal fin.

(iv) *The Hypural Bones* :—(Plate VII. Hy 1 and Hy 2). The fan-like vertical plate formed by the two hypural bones is the terminal part of the vertebral column. The lower hypural (Hy_2) is a triangular plate with a groove at its anterior end, and into this groove fits the bony process on the upper hypural bone (Hy_1). The latter consists of a similar triangular plate having a conical base which is excavated on its anterior face. The rim of this cavity articulates with the similar rim on the posterior side of the 25th vertebra. The urostyle or the upturned rod-like continuation of this centrum-like conical base of the upper hypural is not discernible along its dorsal edge. The posterior edges of these hypural bones are thick and cartilaginous and provide articulation for the caudal fin-rays.

Between the dorsal hypural and the neural spine of the previous vertebra there are two plate-like bones called epurals (Ep_1 and Ep_2). These two appear to complete dorsally the median quadrate bony plate formed by the last vertebra and the hypural bones. The posterior part of the 2nd epural is cartilaginous and to it are attached some caudal fin-rays of the dorsal region.

(v) *The Ribs*:—(Fig. 8 and Plate VII. Fig. 9). There are two kinds of ribs—simple (S. Rib.) and forked (Br. Rib.). The first vertebra (Fig. 8) has got a simple rib attached to the side of the centrum by a ligament. The second vertebra has also got a similar rib but it is attached to the parapophysis at its base. From the third to the 9th vertebra the ribs are forked and attached posteriorly to the bases of the parapophyses. Their bases are slightly concave and their long branches are directed downwards and backwards while their short ones are directed horizontally outwards and backwards. The ribs of the vertebræ from the 10th to the 14th are again simple and attached to the bases of the hæmal arches. They are relatively short and are directed horizontally backwards and outwards.

In passing, it may be mentioned here that the shorter horizontal branches are really the true ribs and their presence in the first five caudal vertebræ indicates that in the embryonic stage the abdominal cavity extended to them. The downward long branches are the representatives of the pleural ribs. In the formation of these forked ribs the horizontal ribs seem to have shifted their articulations from the centra to the pleural ribs.

THE APPENDICULAR SKELETON

(i) *The Pectoral Girdle and the Pectoral Fins* (Plate VIII. Fig. 10). The pectoral arch is a V-shaped arch with its apex situated ventrally and the arms articulating dorsally to the skull in its posterior region. Each arm of the girdle is again bent in the middle so as to bulge obliquely outwards and backwards. It consists of the following bones on each side.

The Post Temporal:—(Plate VIII. Ptm.) This bone also known as the supra-scapula is much forked from its articular surface. Its dorsal limb (D. A. Ptm.) is connected with a flat triangular facet on the epiotic and the ventral limb (V. A. Ptm.) fits into a shallow pit on the opisthotic. Its dorsal limb bears at its base a thin scale-like bony plate (Sc. P.) which covers laterally its joint with the supra-cleithrum (S. Cl.). It is well ossified except at its articular surfaces.

The Supra-cleithrum:—(Plate VIII. S. Cl.). It is an elongated bone, rod-like above and flattened below. Its handle-like upper part has a curved and cartilaginous edge fitting into a corresponding socket on the inner side of the post-temporal. Its ventral part overlaps the dorsal flattened end of the cleithrum with which it is articulated.

The Cleithrum:—(Plate VIII. Cl.). It is an irregular rod-like bone with its upper one-third being flattened and turned forward. Its ventral end is flattened and produced forward so as to have a long and firm joint with its fellow of the other side. It has a plate-like expansion curving round its posterior side and a lateral flat process (La. P.) directed prominently outwards. On its ventro-posterior side there is one protruding condyle (C.Pl.G.) for the articulation of the pelvic girdle. Its posterior expansion in its dorsal part includes the scapula fused with it. The latter is produced downwards posteriorlv and overlaps the short dorsal lamellar process of the coracoid. The scapular foramen (Sc. F.) is bounded dorsally and laterally by the scapula and the cleithrum. To the posterior edge of the scapula are articulated almost all the radials of the pectoral fin.

The Scapula:—(Plate VIII. Sc.). It is not a separate bone but is represented by a part of the posterior extension of the cleithrum in its dorsal half. This laminate part is produced ventrally and overlaps the dorsal portion of the coracoid as noted above,

The Coracoid:—(Plate VIII. Co.). It consists of an anterior handle and a posterior rounded plate dorsally attached to and overlapped by the ventral side of the scapula. It forms the ventral border of the scapular foramen. It is well ossified except at its ends to which is partly attached the fourth radial. Its handle articulates anteriorly with the cleithrum by the side of its condyle for the pelvic girdle.

The Pectoral Fins:—(Plate VIII). The pectoral fins are relatively well developed and very powerful being used as the locomotive organ when the fish is on land. The skeleton of the pectoral fin consists of four flattened radials proximally and thirteen dermal fin rays distally.

The Radials:—(Plate VIII. Ra.). The four elongated and flattened radials form a shallow watch-glass shaped plate which is convex outside and concave inside. Its broad base is lined with cartilage and articulates with the posterior coraco-scapular edge. It narrows towards its distal end which is also lined with cartilage and provides articulation for the dermal fin rays. Its radials appear to have smooth lateral edges but on dissection the second, the third and the fourth are found to be produced into a few teeth in the middle. These teeth fit into corresponding notches on others and thus make up the plate strong and firm.

The Fin Rays.—(Plate VIII). There are eleven articulated and branched fin rays in addition to some short and unbranched ones at the sides. Each typical ray consists of two slender rods which are joined together by their sides in their proximal half through an intervening slender cartilage and become separated and divided in their distal halves. At its base its two rods separate from each other to embrace the articular edge of the radial. At this joint also there is an intervening cartilaginous pad (Sub. C. P.)

(ii) *The Pelvic Girdle and the Pelvic Fins*:—(Plate IX. Figs. 11 and 12). The pelvic girdle is a characteristic and peculiar structure resembling a helmet or topee with broad triangular rim. This complex pelvic girdle can be seen to be made up of two pelvic bones (P. B.) joined to form a V-shaped base and their mesial flanges widening and curving upwards to meet in the middle and to form a dome-like structure on it (Plate IX). The broad and thick anterior edge of the pelvic bone is produced to have a long and vertical joint with the condyle of the cleithrum. Posteriorly the bone bends inwards so as to meet its fellow of the other side in the middle. To the posterior halves of their lateral or outer sides are articulated the pelvic fin rays (P. F.) The arched dome-like flanges of these bones nearly meet in the middle by their toothed and irregular edges (T. Ed.). These plates are not of uniform thickness but have rib-like transverse thickenings. Anteriorly these plates are produced into curved and slender ribs (Fig. 12, Cu. R.) which bend outwards and downwards. The anterior edges of the pelvic bones and these ribs are joined together by a very thick and irregular wall of cartilage. Laterally this thick cartilage on each side between the upturned anterior edge of the pelvic and the end of the anterior bony rib of the flange, provides a socket (So.) for articulation with the condyle on the pectoral girdle. Ventrally it is produced and firmly attached to the posterior edge of the jointed cleithra. From the ventral side of the fish, the pelvic girdle with its anterior cartilaginous wall shows a bowl-like cavity (Fig. 12. Bw. C.). Two slender bony ribs (B. R.) arising from the mesial edges of the flanges of the pelvic bones curve downwards and reach the level of the mouth of its dome-like cavity. Here they are joined by two transverse straight strips (B. S.) of cartilage from its sides and by a ventral ligamentous partition from the middle of its anterior wall. The latter is supported ventrally by a slender bony rod. (Fig. 12. R. Li. Pa.).

Pelvic Fin Rays:—Each pelvic fin has got one strong spine and five branched and articulated fin-rays. The two fins are situated very close together and joined basally. These basal edges are strengthened by small cartilaginous pads.

(iii) *The Median Fin Rays*:—(Fig. 8). The fish has four median fins. The skeleton in the case of the two dorsals ($D.F_1$ & $D.F_2$) and the anal fin (A. F.) consists of a series of trisegmented radials or basal elements and long dermal fin rays. The skeleton of the caudal (C. F.) resembles that of the pelvic and pectoral fins.

(a) *The First Dorsal Fin*:—(Fig. 8. D. F.). Its fin rays (Sp.) are spinous and flexible. The first spine is nearly as long as the height of the fish and the remaining spines become gradually shorter posteriorly. Each of them is bifurcated at the base (B. B.) thereby forming a groove between them. The bifurcated ends bear condyles which rest on the lateral projections on the dorsal part of the radial. The bottom of the groove formed between them rests on the bottom of the groove present on the dorsal side of the radial. The first four of these spines are articulated with the first four radials (Ra.) situated in between the neural spines. These radials being much compressed laterally and expanded antero-posteriorly join to form a median vertical bony plate occupying the inter-spaces between the third and the fourth, and between the fourth and the fifth neural spines. In their radial elements can be distinguished only the large bony proximal (Pr. Seg.) and cartilaginous nodule-like distal segments (Di. Seg.) as are found in typical bony fishes. The middle segment is either absent or might have early fused with the proximal. The dorsal edge of the first radial is notched in the middle and produced into lateral flaps to support the two lateral condyles at the base of the first spine. From the second backwards upto the fourth the notch is situated at its anterior end and thus the spine articulates also with the distal cartilaginous segment of the anterior radial. The 5th, the 6th and the 7th fin rays are without any radials to support them. There is one more radial behind (R_5) in the form of a bent slender rod situated above the 6th and the 7th neural spines and supporting the last three fin rays.

(b) *The Second Dorsal Fin* :—(Fig. 8. D, F. 2). Its skeleton consists of one spine and twelve branched fin rays supported by fourteen radials in all. The first three radials situated above and in between the tenth and the eleventh, and the eleventh and the twelfth neural spines support the first spinous ray and the last radial situated in front of the 19th vertebra supports the eleventh and the twelfth fin rays. Each of the remaining fin rays articulates with its corresponding set of radials. The latter consists of a long bony proximal, (Pr. Seg.) a short bony middle (M. Seg.) and a nodular cartilaginous distal segment (Di. Seg.). The fin ray is distally segmented and branched and at the base dilated and cleft. It firmly rest on the proximal segment of its radial and articulates and embraces the distal segment of the radial in front. There is one accessary distal segment (Ac. Dis. Seg.) in front of the spine which is taken as the first radial of the second dorsal fin.

(c) *The Anal Fin* :—(Fig. 8, A. F.). Its skeletal elements are similar to those of the second dorsal. They are situated below and between the thirteenth and the eighteenth hæmal spines. The first fin ray is rudimentary, being very short and nodular, but has got an accessary radial to support it as the spine of the second dorsal. Anteriorly the fin rays are short but become gradually longer posteriorly like those of the second dorsal, but on the whole they are shorter than those of the latter.

(d) *The Caudal Fin* :—(Fig. 8, C. F.) The skeleton of the caudal fin consists of only fourteen fin rays and the place of the radial is taken up by the hypural bones (Hy_1& Hy_2) of the vertebral column. Each of them consists of two lateral rods joined together in their middle third and segmented and seperated in the rest. They articulate with the posterior fibro-cartilaginous edge of the hypural bones like those of the pectoral fins. The caudal fin has narrow thin strip-like prolongations anteriorly on the dorsal and ventral sides and are continued a little further in the form of loose folds of the skin. These are supported by very short rudimentary fin rays which are without any radials to support them. The fin rays on the dorsal side project a little beyond the edge and become shorter anteriorly. Those of the ventral fold are similarly short and rudimentary but do not reach the margin of the fin-like fold of the skin.

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PLATE VI

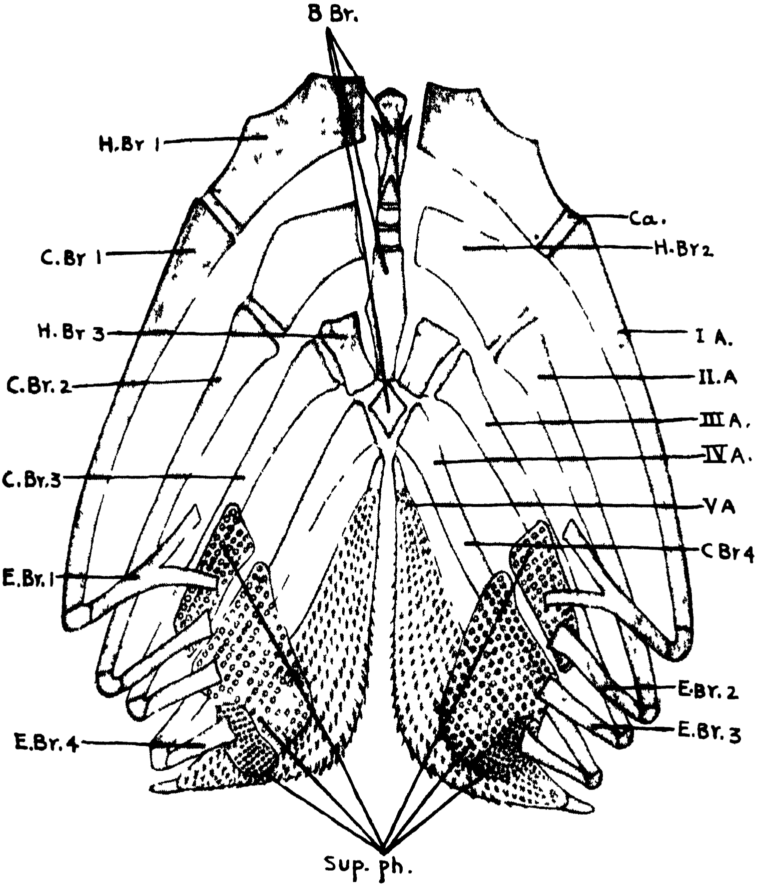

FIG. 7.

Dorsal View of the Branchial Apparatus with the Suprapharyngeals slightly stretched aside.

I. A. = First branchial arch; II. A. = Second branchial arch; III. A. = Third branchial arch; IV. A. = Fourth branchial arch; V. A. = Fifth branchial arch; B. Br. = Basibranchial; Ca. = Cartilage; C. Br$_1$ = First ceratobranchial; C. Br$_2$ = Second ceratobranchial; C. Br$_3$ = Third ceratobranchial; C. Br$_4$ = Fourth ceratobranchial; E. Br$_1$ = First epibranchial; E. Br$_2$ = Second epibranchial; E. Br$_3$ = Third epibranchial; E. Br$_4$ = Fourth epibranchial; H. Br$_1$ = First hypobranchial; H. Br$_2$ = Second hypobranchial; H. Br$_3$ = Third hypobranchial; Sup. Ph. = Suprapharyngeal.

PLATE VII

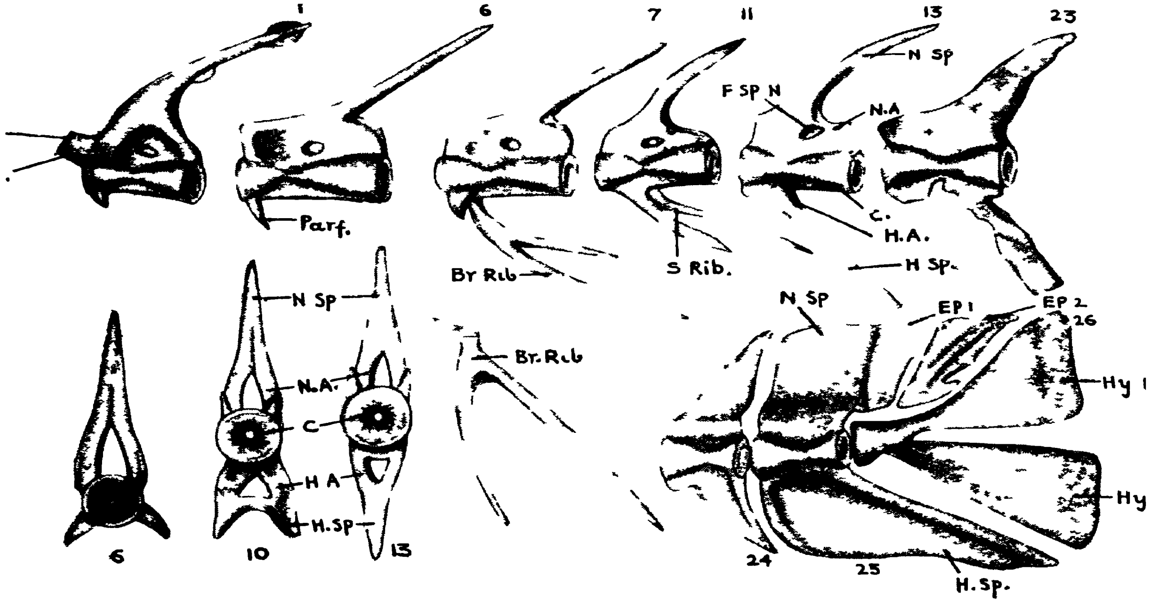

FIG. 9. Typical Vertebræ.

Br. Rib = Branched rib ; C. = Centrum ; Ep_1 = First epural ; Ep_2 = Second epural ; Fa = Facet ; F. Sp. N. = Foramen of the spinal nerve ; H. A. = Hæmal arch ; H. Sp. = Hæmal spine ; Hy_1 = First hypural , Hy_2 = Second hypural ; N. A. = Neural arch N. Sp. = Neural spine ; Parf. = Parapophysis ; Pr. = Process ; S. Rib. = Simple rib.

PLATE VIII

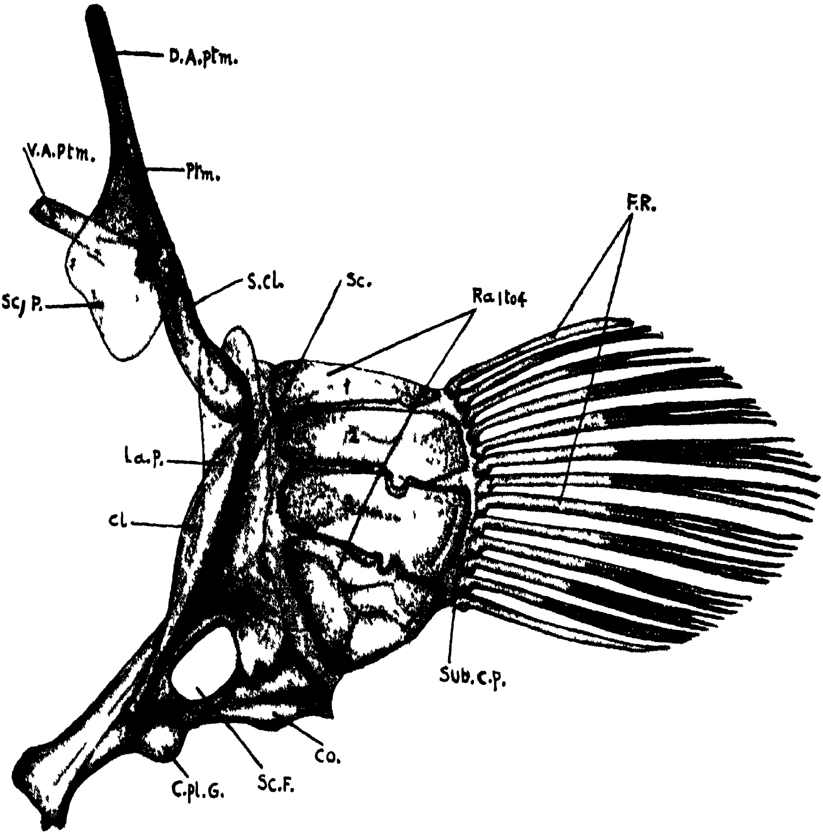

FIG. 10.

Lateral View of the Pectoral Girdle with the Pectoral Fin.
(of one side).

Cl. = Cleithrum ; Co. = Coracoid ; C. Pl. G. = Condyle for the pelvic girdle ; D. A. Ptm. = Dorsal arm of the post-temporal ; F.R. = Fin rays ; Ptm. = Post-temporal ; Ra. = Radials ; S. Cl. = supra cleithrum ; Sc. = Scapula ; Sc. P. = Scale-like bony plate ; Sc. F. = Scapular foramen ; Sub. C. P. = Sub-cartilaginous pad : V. A. Ptm. = Ventral arm of the post-temporal.

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do.	Study of the effect of omission of Red and Blue Violet Rays from the white light on formation of carbohydrates in leaves.	Mr. R. B. M. Colah.	Prof. R. H. Dastur and Prof. R. E. Cooper	Royal Institute of Science, Bombay	
do.	The effect of a Mixture of 2 parts of Blue-Violet and one part of white light on the formation of carbohydrates in leaves.	Mr. R. R. Ullal.	do.	do.	
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